

PROCEEDINGS
OF THE
NATIONAL ACADEMY OF SCIENCES
INDIA

1957

VOL. XXVI

SECTION A

PART II

MARCH 1957



NATIONAL ACADEMY OF SCIENCES, INDIA
ALLAHABAD

THE NATIONAL ACADEMY OF SCIENCES, INDIA

(Registered under Act XXI of 1860)

Founded 1930

Council for 1957

President

Prof. P. S. Gill, M.S., Ph.D., F.A.P.S., F.N.I., F.N.A.Sc., Aligarh.

Vice-Presidents

Prof. N. R. Dhar, D.Sc., F.R.I.C., F.N.I., F.N.A.Sc., Allahabad.

Prof. W. D. West, M.A., C.I.E., Sc.D., F.A.S., F.N.I., F.N.A.Sc., Saugor.

Honorary Treasurer

Prof. S. Ghosh, D.Sc., F.R.I.C., F.N.I., F.N.A.Sc., Allahabad.

Foreign Secretary

Dr. R. K. Saksena, D.Sc., F.N.I., F.N.A.Sc., Allahabad.

General Secretaries

Dr. R. N. Tandon, M.Sc., Ph.D., D.I.C., F.N.A.Sc., Allahabad.

Shri S. Basu, M.Sc., F.N.I., F.N.A.Sc., New Delhi.

Members

Prof. P. L. Srivastava, M.A., D.Phil., F.N.I., F.N.A.Sc., Allahabad.
Mrs. Savitri Sahni, M.Sc., F.N.A.Sc., Lucknow.

Prof. S. Ranjan, M.Sc., D.Sc., F.N.I., F.N.A.Sc., Allahabad.

Prof. A. K. Bhattacharya, D.Sc., F.R.I.C., F.N.A.Sc., Saugor.

Prof. K. Banerji, D.Sc., F.N.I., F.N.A.Sc., Allahabad.

Prof. R. Misra, M.Sc., Ph.D., F.N.I., F.N.A.Sc., Banaras.

Prof. M. D. L. Srivastava, D.Sc., F.N.A.Sc., Allahabad.

Shri M. S. Randhawa, M.Sc., F.N.I., F.N.A.Sc., I.C.S., New Delhi.

Prof. H. R. Mehra, M.Sc., Ph.D., F.N.I., F.N.A.Sc., Allahabad.

The Proceedings of the National Academy of Sciences, India, is published in two sections: Section—A (Physical Sciences) and Section—B (Biological Sciences). Six parts of each section are published annually.

The Editorial Board in its work of examining papers received for publication is assisted, in an honorary capacity, by a large number of distinguished scientists. Papers are accepted from members of the Academy *in good standing*. In case of a joint paper, one of the authors must be a member of the Academy. The Academy assumes no responsibility for the statements and opinions advanced by the authors. The papers must conform strictly to the rules for publication of papers in the *Proceedings*. A total of 50 reprints are supplied free of cost to the author or authors. The authors may have any reasonable number of additional reprints at cost price, provided they give prior intimation while returning the proof.

Communications regarding contributions for publication in the *Proceedings*, books for review, subscriptions, etc., should be sent to the General Secretary, The National Academy of Sciences, India, Lajpatrai Road, Allahabad-2 (India).

Annual Subscription for each Section: Rs. 30 (Inland); 60 sh. (Foreign)
Single Copy: Rs. 5 (Inland); 10 sh. (Foreign).

PROCEEDINGS
OF THE
NATIONAL ACADEMY OF SCIENCES
INDIA

1957

PART II]

SECTION A

[VOL. XXVI

CORONA RELATIONSHIP UNDER LOW FREQUENCY
SILENT ELECTRIC DISCHARGE

BY D. P. JATAR AND H. D. SHARMA

(*Department of Physics, University of Saugar*)

Received on February 23, 1957

ABSTRACT

The corona relationship is investigated for l.f. silent electric discharge in air in the range of pressure from 1-250 mm. Hg, using Maze counter type discharge tubes. The corona relationship is found to hold if a correction is made for the fall of potential on the glass walls.

INTRODUCTION

FOR d.c. discharges between coaxial metal cylinders it is known¹ that in cases where the coefficients of ionization are very small at points remote from the inner cylinder, the corona breakdown potential with a given wire of radius r varies with the cylinder radius R in such a way as to maintain the field X at the wire constant. This 'corona relationship' has recently been extended^{2,3} to a.c. discharges using metal electrodes under certain conditions. Studies in air and hydrogen under sleeve excitation and using plane parallel glass electrodes indicated^{4,5} that the threshold potential for the l.f. silent electric discharge is identifiable with the corresponding Paschen potential, as suggested by Joshi,⁶ though the threshold potential values are higher corresponding to a fall of potential on glass. It was therefore of interest to

investigate if the corona relationship could be extended to the case of glass electrodes also.

EXPERIMENTAL

Six discharge tubes, essentially similar to Maze counters, consisting of a central copper wire electrode of diameter ($2r$) 0.5 mm. each, mounted coaxially in glass cylinders of external diameter ($2R$) 0.69, 0.785, 0.94, 1.41, 2.03 and 2.63 cm. respectively, were excited by an H.T. transformer using 50 cycles a.c., a bare copper wire wound tightly round the outer glass cylinder serving as the other electrode. Laboratory air, filtered through glass wool and dried over CaCl_2 and P_2O_5 , was used in the range of pressure ' p ' from 1-250 mm. Hg. The threshold potential, V_m , was taken as that critical potential at which there were (i) a sudden rise in the current flowing through the discharge tube, as measured by a galvanometer in the plate circuit of a current detector (1 H5GT) connected to the L.T. line across a resistance; (ii) the initiation of a glow characteristic of the gas in the discharge tube, and (iii) the appearance of h.f. pulses on the current wave form investigated by feeding the potential drop across a serial resistance in the L.T. line to the vertical input of the cathode-ray oscillosograph.

It is of interest to note here that even with metal electrodes the breakdown in air is known^{1,3} to be erratic making measurements more difficult than in other gases. A similar difficulty was encountered in the present work also. It was found that a fresh tube always behaved more erratically than an aged one and observations were made only after the tubes had been aged for a minimum of 30 minutes. However, this 'ageing' treatment was not always enough, and long and intermittent ageing was found to yield better results.

RESULTS

Figure 1 shows the variation of the threshold potential, V_m , (KV, a.c. peak value) with ' rp ' (mm. Hg cm.) for the different tubes used. It is seen that the curves are essentially similar to those using metal electrodes under d.c. excitation, the curves being concave towards the ' rp ' axis. The influence of reducing the diameter of the outer cylinder, while keeping the wire diameter constant, is to decrease V_m .

Figure 2 A shows the variation of rX with rp taking the inner diameter of the outer glass cylinder for the calculation of rX , as in metal electrodes. The results, using the outer diameter for the calculation of rX , are shown in Fig. 2 B. It is seen that while the $rX-rp$ curves appear to coincide for low values of rp , there is a marked divergence for the higher values of rp . A comparison reveals that the divergence is appreciably less (max. $\pm 7\%$)

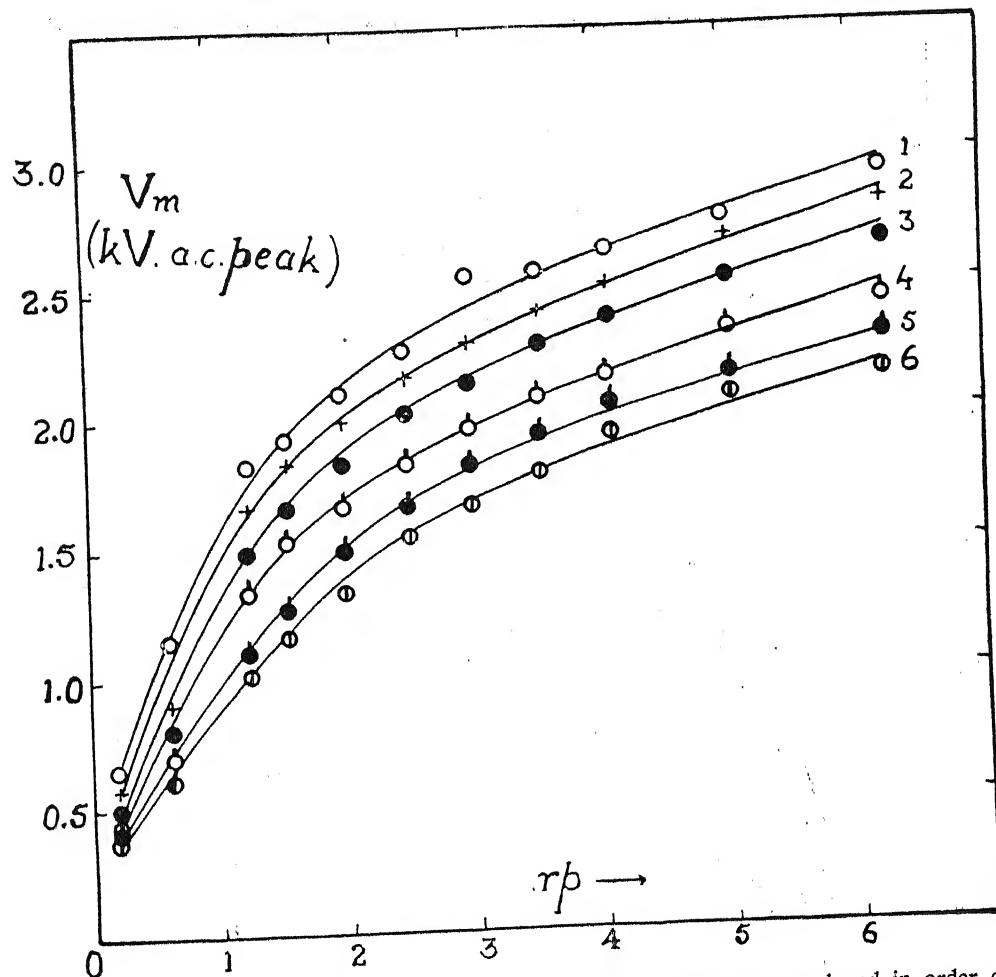


FIG. 1. Variation of threshold potential V_m with rp . Curves are numbered in order of decreasing diameter of the glass cylinder for all figures.

when the outer diameter is used for calculation as compared with that (max. $\pm 14\%$) when the inner diameter is used.

DISCUSSION

Corona studies using point-to-plane and wire-in-cylinder geometries in air have been reported by a number of workers.^{7,8} Since the corona onset is dependent on the parameter $X|p$, it is to be expected that, with a constant gap, V_m would vary linearly with pressure (or rp since r is constant). From the data available in literature,^{1-3,7,8} however, it is seen that the onset potential is not a linear function of the gas pressure in the case of corona discharges. The theory for the corona thresholds has recently been worked out

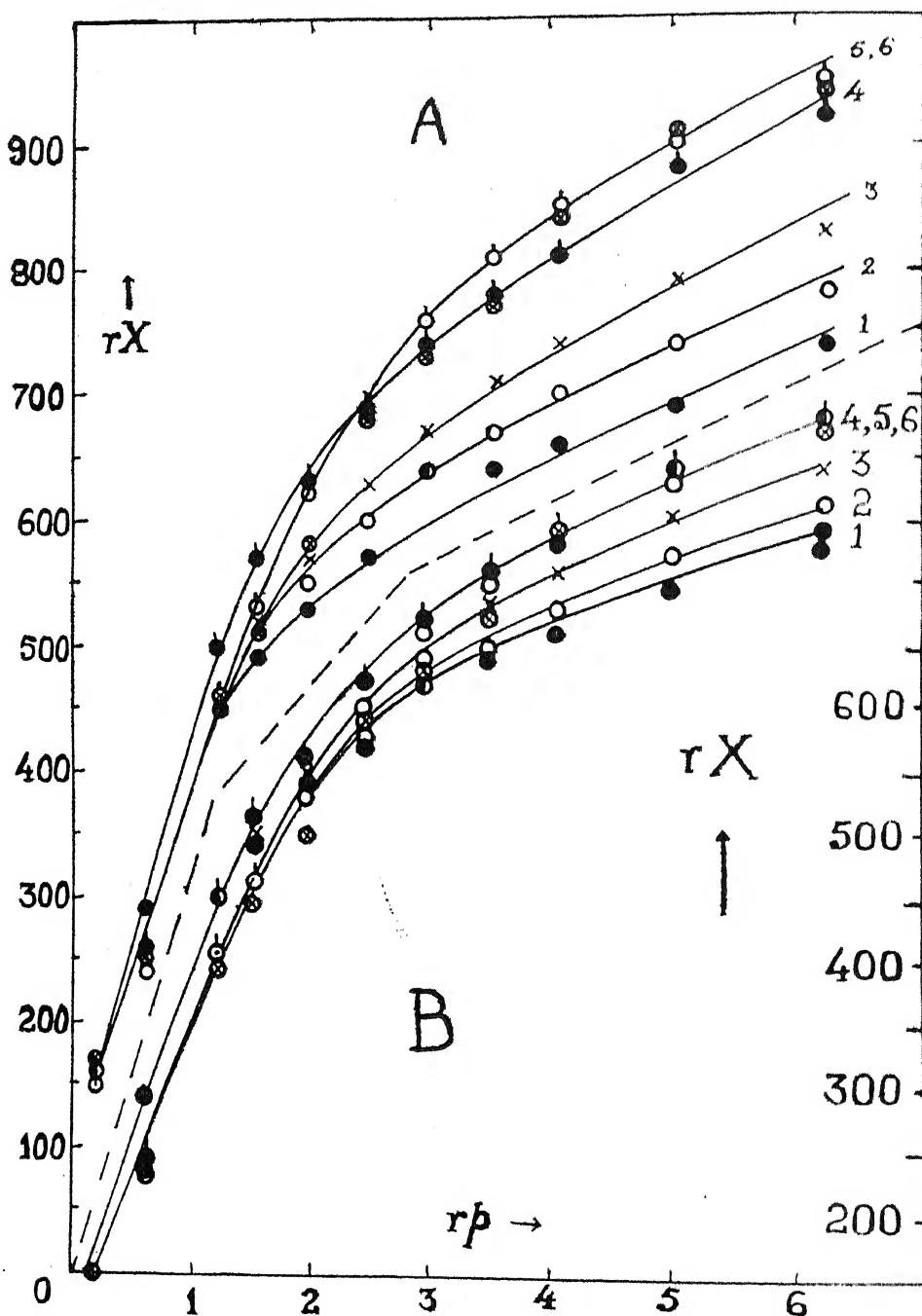


FIG. 2. A. Corona relationship using inner diameter of glass cylinder for calculation of rX . B. Corona relationship using outer diameter of glass cylinder for calculation of rX .

by Loeb⁹ and his results indicate that the curves need not be linear. Corona breakdown in air under high frequency excitation has recently been reported by Jones and Morgan³ and their results indicate that the breakdown potential is appreciably lower for a smaller tube. The present results are in accord with this.

The corona relationship under d.c. excitation has been investigated by a number of workers.^{1,10} Recently Craggs and Meek² have shown that the 50 cycle a.c. onset potentials are equal to the corresponding d.c. onset potential and the corona relationship holds even for 50 cycle a.c. excitation provided the radius of the outer electrode R is appreciably larger than the radius of the wire r . Essentially similar results are reported by Jones and Morgan³ recently for air under h.f. excitation. All these studies refer to metal electrodes where the potential applied to the electrodes is completely operative on the gas phase, the metal being an equipotential surface. That the same considerations cannot be applied to the case of glass electrodes is seen from Fig. 2 A, where the curves show a wide divergence (max. $\pm 14\%$). This is in accord with the results^{4,5} in air and hydrogen under sleeve excitation and using plane parallel glass electrodes, that the fall of potential on the glass walls is appreciably larger than an equal thickness of gas. Assuming the glass walls to be replaced by an equal thickness of gas, the results, shown in Fig. 2 B, reveal that the $rX-rp$ curves agree appreciably better, the divergence being not greater than $\pm 7\%$ throughout the rp range investigated.

It is of interest to note here that rX goes on increasing as the diameter of the outer cylinder is diminished, that for the smallest tube used being the largest. An essentially similar result is reported by Jones and Morgan³ using two tubes in air under h.f. excitation, though their rp range is appreciably smaller. It may be pointed out here that, contrary to the findings of other workers^{1,10} who observed better agreement for higher pressures using metal electrodes, the spread of values in the present case is found to be appreciably larger for higher rp values, *i.e.*, for higher pressures (the percentage variation changing from about $\pm 2\%$ to $\pm 7\%$).

The fall of potential on glass, however, being larger than an equal thickness of gas, calculations were also made by taking the equivalent thickness of air to be 25% larger than the thickness of the glass walls and the results are shown in Fig. 3. It is seen that the agreement is much better for higher rp values, the divergence being only about $\pm 4\%$ which is within the experimental error ($\pm 5\%$). However for smaller rp values the divergence is greater (about $\pm 6\%$). This is in accord with other workers in the field.^{1,10} Moreover, rX for smaller tubes is still found to be slightly larger than that for

larger tubes.³ It may be emphasized here that the percentage increase chosen here is arbitrary, and the results using other percentages are not shown here.

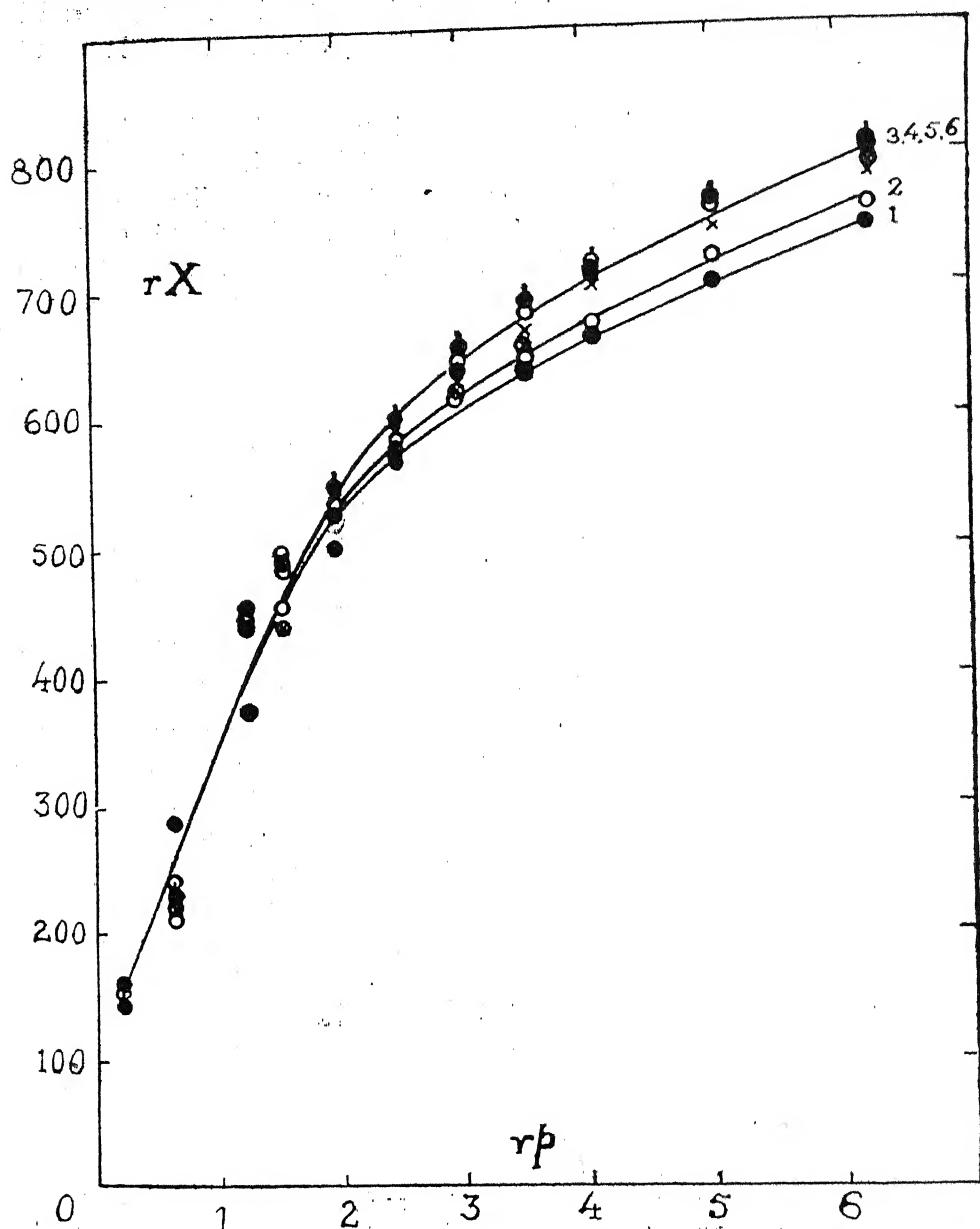


FIG. 3. Corona relationship on replacing glass wall thickness by a 25% larger thickness of air.

It is significant to note here that the corona relationship maintaining X (and hence rX) at the wire constant holds good provided $R > Ru$, where Ru is the radius of the cylindrical volume coaxial with the wire within which the discharge is confined. The above condition appears to be fulfilled for higher rp values and the corona relationship holds good within experimental error. For lower rp values for very small R tubes, the discharge seems to spread in the entire region leading to higher values of rX for smaller tubes. It is to be concluded that the corona relationship holds good for this type of discharge also for higher rp values provided a proper correction for the fall of potential on the glass walls is made.

Our thanks are due to Dr. D. R. Bhawalkar for providing the necessary facilities to carry out this work.

REFERENCES

1. TOWNSEND, 1947, *Electrons in Gases*, Hutchinson's Scientific Publications.
2. JONES, 1953, *Rep. Progr. Phys.*, **16**, 216 (*Phys. Soc., London*).
2. CRAGGS AND MEEK, 1948, *Proc. Phys. Soc. (Lond.)*, **60**, 327.
3. JONES AND MORGON, 1951, *ibid.*, **64 B**, 560.
____ AND WILLIAMS, 1953, *ibid.*, **66 B**, 17.
____, See also Jones Ref. 1.
4. JATAR, 1956, *Ph.D. Thesis*, B.H.U. 1951; 1956, *Proc. Nat. Acad. Sci. (India)*, **25 A**, 38.
5. ____ AND SHARMA, 1955-56, *Saug. Univ. Journ.*, **1**, (5), 103.
____, 1956, *J. Sci. Indust. Res.*, **15 B**, 417.
6. JOSHI, 1939, *Curr. Sci.*, **8**, 548; *Proc. Ind. Acad. Sci.*, 1942, **22 A**, 389.
7. TRICHEL, 1938, *Phys. Rev.*, **54**, 1078; 1939, **55**, 382.
KIP, 1938, *ibid.*, **54**, 139; 1939, **55**, 549.
WEISSLER, 1943, *ibid.*, **63**, 96.
FITZSIMMONS, 1942, *ibid.*, **61**, 175.
8. MORTON, 1946, *ibid.*, **70**, 358.
JOHNSON, 1948, *ibid.*, **73**, 284.
ENGLISH, 1947, *ibid.*, **71**, 638; 1948, **74**, 170.
9. LOEB, 1948, *J. Appl. Phys.*, **19**, 882.
10. HUXLEY, 1928, *Phil. Mag.*, **5**, 721; 1930, **10**, 185.
BRUCE, 1930, *ibid.*, **10**, 476.
HUXLEY AND BRUCE, 1937, *ibid.*, **23**, 1096.

STUDIES IN COAGULATION

Part VII. Nature of Hydrous Stannic Oxide and Coagulation of Its Positive Sol

BY RAMA SHANKER RAI AND SATYESHWAR GHOSH

(*Chemical Laboratories, University of Allahabad*)

Received on May 10, 1957

ABSTRACT

Hydrous stannic oxide is amphoteric in nature. Its basic property is enhanced in acid medium, whilst it develops acidic character in alkaline medium. If a sol of hydrous stannic oxide in acid medium is taken and coagulated by electrolytes, adsorption of the hydrogen-ions takes place making the solution less acidic. Positively charged sol of hydrous stannic oxide is not, however, very stable possibly due to quick ageing. When a dilute solution of stannic chloride is left over, a white gelatinous precipitate collects.

It has been observed¹ that a sol of hydrous stannic oxide peptized by ammonia liberates considerable amount of acid, when coagulated by electrolytes, because the hydrous oxide develops acidic character in alkaline medium and is capable of adsorbing hydroxyl ions. The hydrous oxide is charged positively in acid medium due to its amphoteric nature.² But the ageing of the positively charged hydrous stannic oxide sol being very quick, it is not possible to obtain a very stable sol. Therefore, it was thought necessary to investigate a freshly formed positively charged sol of hydrous stannic oxide.

EXPERIMENTAL

The following experiment was performed to find out the nature of the hydrous stannic oxide regarding the changes in the $[H^+]$ and $[OH^-]$ ions in the presence of an electrolyte.

30 ml. suspension of well-washed hydrous stannic oxide was acidified with hydrochloric acid or, it was made alkaline by adding ammonia. The quantity of acid or alkali varied in all the samples, though the volumes were kept constant by adding distilled water. 20 ml. of each sample were taken and the volume was made 25 ml. by adding 5 ml. 0.4 N potassium sulphate and the pH of the samples were measured by a cambridge portable pH meter in conjunction with a glass electrode supplied by the manufacturers. The results for such measurements are given in Table I.

A solution of stannic chloride was taken and caustic soda was added to it. 10 ml. of the sample was taken each time and the volume was made to 20 ml. by the addition of potassium sulphate and distilled water. pH of the samples were measured and the results are given in Table II.

Samples A-H are prepared by adding hydrochloric acid and samples A'-D' by adding ammonia to the precipitate.

TABLE I

Sample	pH after adding	
	Water 5 ml.	K ₂ SO ₄ 5 ml.
A	0.9	1.0
B	1.2	1.3
C	1.4	1.5
D	1.7	1.9
E	2.2	2.5
F	2.6	3.2
G	3.1	3.7
H	5.0	5.0
A'	10.8	11.0
B'	10.5	10.7
C'	10.4	10.6
D'	10.3	10.3

TABLE II

K ₂ SO ₄ in ml. 0.4 N	pH	
	Fresh sample	4 days aged sample
0	0.80	0.82
1	0.84	1.00
2	0.86	1.04
3	0.88	0.92*
4	0.90	0.88
5	0.92*	0.82
6	0.86	0.94
7	0.86	0.94
8	0.92	0.94
9	0.94	0.94
10	0.94	0.94

* Complete coagulation takes place.

DISCUSSION

The difference in the changes in the hydrogen-ion concentration of the samples in the presence of water and potassium sulphate are plotted against pH and the curve is given in Fig. 1. It gives the range of pH where neither acid nor alkali is liberated. It has already been observed that the

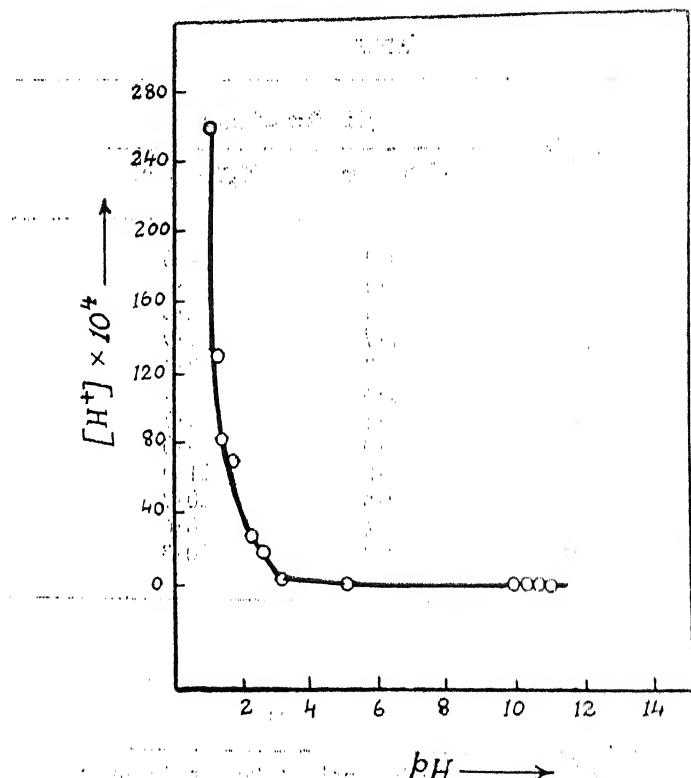


FIG. 1. Variation of $[H^+]$ liberated with change in pH of the sol.

adsorption of hydrogen-ions produces alkali³ and that of OH^- ions increases hydrogen-ions¹ in the sol medium. Obviously the former is due to the basic character, while the latter is due to the acidic character of the hydrous oxide. Hence it may be concluded that the isoelectric point of hydrous stannic oxide lies between pH 4-pH 10, and it is approximately at pH 7. Our results are confirmed by the observation of B. N. Ghosh,⁴ who noted that α - and β -oxides of tin, when shaken with salt solutions, liberated acid.

We have observed that a negatively charged sol of the hydrous stannic oxide produces acid on the stepwise addition of electrolytes. We have also observed³ that alkali is generated in the system when a positively charged

sol is coagulated by potassium sulphate. Our results in the case of the positively charged sol of hydrous stannic oxide are quite in agreement with that of positively charged hydrous ferric oxide sol. But in this case the process becomes complicated owing to the hydrolysis, etc.; and on ageing the system becomes more alkaline. The increase in the alkalinity may be explained according to the scheme of coagulation, which suggests the adsorption of H^+ ions by the colloidal particles during the course of the charge neutralization and liberation of OH^- ions in the sol medium.

Our thanks are due to the Ministry of Education, Government of India, for the award of the Senior Research Training Scholarship to one of us (R. S. Rai).

REFERENCES

1. RAI AND GHOSH, 1957, *Kolloid-Z.*, **154**, 146.
2. WEISER, 1935, *Inorganic Colloid Chemistry*, Vol. II. John Wiley and Sons (New York).
3. RAI AND GHOSH, 1955, *Kolloid-Z.*, **142**, 104.
4. GHOSH, B. N., 1928, *J. Chem. Soc.*, 3027.

PHYSICO-CHEMICAL STUDIES IN THE FORMATION OF CUPRAMMONIUM COMPOUNDS

Part II. Composition of Cupric-Ammino Nitrates*

BY ARUN K. DEY

(Chemical Laboratories, University of Allahabad)

Received on October 7, 1957

ABSTRACT

The composition of cupric-ammino nitrates has been studied by electrical conductance and spectrophotometric methods. The existence of tri-, tetra-, penta- and hexa-ammoniates of cupric nitrate has been inferred in an ammoniacal solution of cupric nitrate, the composition of the ammine depending upon the concentration of ammonia present.

IN Part I of the series,¹ the formation of cupric-ammino sulphates in solution has been described, studied by electrical conductance and light absorption studies. In previous communications, the author has described the preparation of cupric pentamminosulphate² and also reported the existence of cupric hexamminosulphate.³ It may be interesting to recall that the colloidal nature of cuprammonia solutions was emphasized by Grimaux,⁴ Dhar and coworkers⁵ and Bhatnagar and collaborators.⁶ In a paper, Dey⁷ generalised the view of the colloidal nature of complex forming systems, obtained by dissolving an insoluble substance in a suitable solution and opined that in such systems, complex ions are the main product only in the presence of an excess of the solvent solution.

In this paper, the investigation of the system $\text{Cu}(\text{NO}_3)_2 - \text{NH}_3 - \text{H}_2\text{O}$, by spectrophotometric and electrical conductance measurements has been recorded.

EXPERIMENTAL

For the determination of electrical conductance, Hartman and Braun's Roller Bridge was used. The induction coil was worked by an accumulator giving not less than 2 volts. A standard L & N resistance box was used. The cell was immersed before and during measurements in a thermostat maintaining $30^\circ \pm 0.1^\circ \text{C}$. The cell constant at different positions of the bridge wire was determined in order to take into account the disuniformity

* A preliminary communication appeared in *Nature*, 1946, 158, 95.
98

of the bridge wire and the calibration curve was used to calculate the conductance.

A standard solution of cupric nitrate BDH AnalaR was prepared and diluted to M/50. Merck's ammonia solution was standardised and diluted to the required extent. To 5 ml. of the cupric nitrate solution were added varying concentrations of ammonia (total volume 10 ml.) and the conductance determined.

The extinction coefficients of the mixtures of different compositions were determined by means of a Nutting's Spectrophotometer (Adam Hilger). The extinction coefficient is given by Bunsen and Roscoe's formula⁸:

Extinction coefficient = D/t , where $D = 2 \log \tan\theta$, θ being the reading on the angle scale. In our case, the scale gave the extinction coefficient directly and the thickness t of the solution was 1 cm. For these studies, M/20 cupric nitrate was used and the extinction coefficients determined between 5,200–6,800 Å.U. The experiments were performed at 30° C.

TABLE I
Electrical conductance of CuNO₃ – NH₃ system

Ratio Cu : NH ₃	Sum of the conductance of reactants × 10 ⁴ mhos	Observed conductance of mixture × 10 ⁴ mhos	Difference × 10 ⁴ mhos	Percentage difference
1: 10	28.55	28.57	0.02	0.07
1: 9.1	28.40	28.42	0.02	0.07
1: 8.3	28.36	28.38	0.02	0.07
1: 7.7	28.32	28.35	0.03	0.11
1: 7.1	28.23	28.26	0.03	0.11
1: 6.7	28.13	29.33	1.20	4.27
1: 6.25	28.04	30.31	2.27	8.09
1: 5.55	27.72	29.36	1.57	5.65
1: 5.00	27.67	28.68	1.01	3.65
1: 4.55	27.33	28.93	1.60	5.85
1: 4.17	27.24	29.69	2.45	8.99
1: 3.85	27.10	29.42	2.32	8.56
1: 3.57	29.96	29.18	2.22	8.22
1: 2.94	26.85	30.10	3.25	12.10
1: 2.38	26.67	29.07	2.40	8.97
1: 2.00	26.58	26.60	0.02	0.75
1: 1.67	26.48	23.68	-2.80	-10.57
1: 1.25	26.36	23.30	-3.06	-11.60
1: 1.00	26.21	23.08	-3.13	-11.94

RESULTS AND DISCUSSION

It is well known that physical properties of mixtures not reacting chemically are additive. Hence, any difference between the sum of the conductivities of the constituents and the observed conductance of the mixture suggests a chemical interaction between the constituents. Any such change of conductance observed in the system $\text{Cu}(\text{NO}_3)_2$ - NH_3OH is ascribed to complex formation. In the following table, we have compiled the percentage difference in conductivity due to complex formation between cupric nitrate and ammonia.

From the above values a graph has been plotted showing the variation of conductance against composition, as may be seen in Fig. 1. The curve shows sharp breaks at 3, 4, 5 and 6 NH_3 per mole of $\text{Cu}(\text{NO}_3)_2$, showing the existence of these ammoniates in solution.

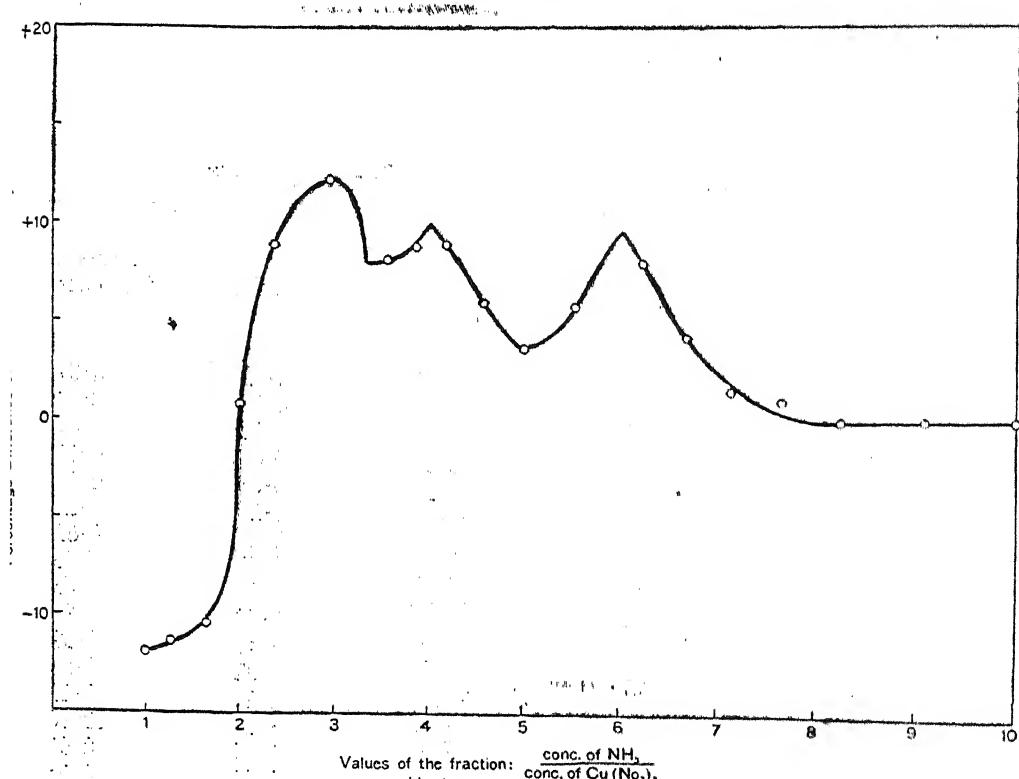


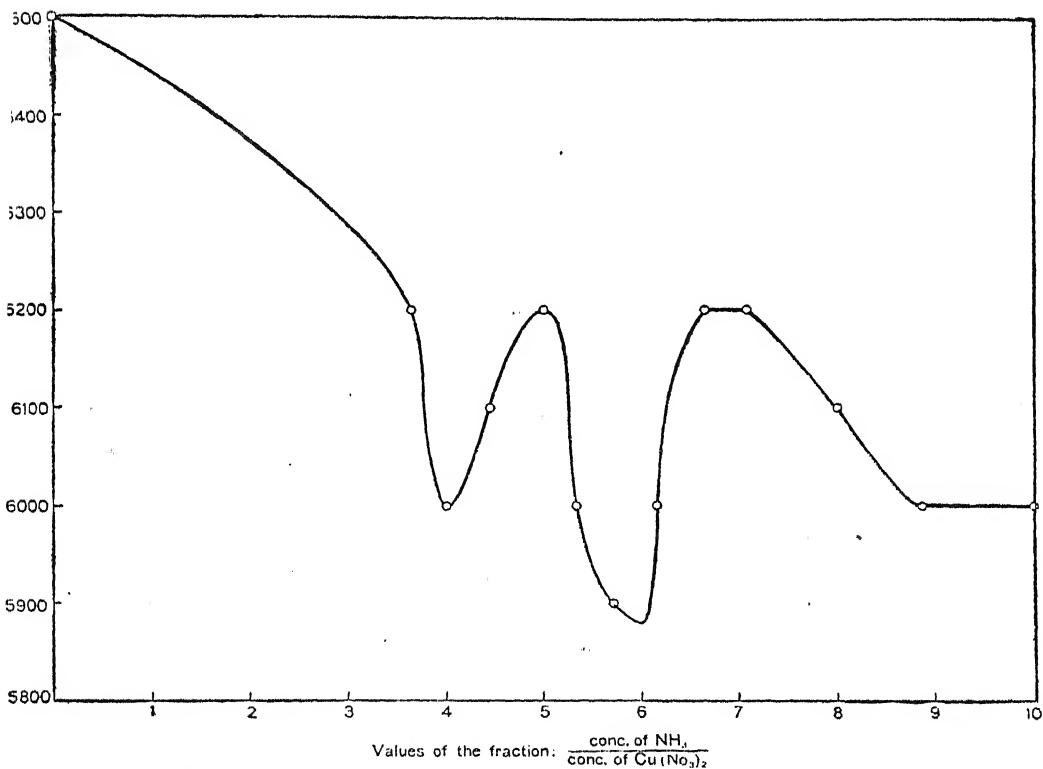
FIG. 1. Conductometric Study of $\text{Cu}(\text{NO}_3)_2$ - NH_3 system.

From the values of the extinction coefficients of the various mixtures at different wave-lengths, the values of λ_{max} , corresponding to the composition of the mixtures, are compiled in Table II.

TABLE II
Light absorption by $Cu(NO_3)_2-NH_3$ system

Ratio Cu : NH ₃	λ_{\max} in Å.U.
1: 0	6500
1: 3.64	6200
1: 4.00	6000
1: 4.44	6100
1: 5.00	6200
1: 5.33	6000
1: 5.72	5900
1: 6.15	6000
1: 6.67	6200
1: 7.09	6200
1: 8.00	6100
1: 8.89	6000
1: 10.0	6000

The composition – wave-length graph (Fig. 2) shows sharp breaks corresponding to 4, 5 and 6 moles of NH₃ per Cu, indicating the formation

FIG. 2. Spectrophotometric Study of $Cu(NO_3)_2-NH_3$ system.

of the corresponding ions in solution. The formation of tri-ammoniate is not indicated here, as the solution with 3 NH₃ is too turbid to allow a measurement of the extinction coefficient.

REFERENCES

1. DEY, A. K. AND BHATTACHARYA, A. K., 1952, *Z. Phys. Chem.*, **200**, 23.
2. —————, 1946, *Proc. Ind. Acad. Sci.*, **23A**, 259.
3. DEY, A. K., 1947, *Nature*, **159**, 333.
4. GRIMAUX, 1884, *Compt. Rend.*, **87**, 1434.
5. DHAR, N. R. AND COWORKERS, 1920, *Trans. Farad. Soc.*, Oct. 1920;
J. Phys. Chem., 1920, **27**, 376.
6. BHATNAGAR, S. S. AND COLLABORATORS, 1928, *Kolloid-Z.*, **44**, 79.
7. DEY, A. K., 1948, *J. Colloid Sci.*, **3**, 473.
8. BUNSEN AND ROSCOE, 1857, *Pogg. Ann.*, 235.

PHYSICO-CHEMICAL STUDIES IN THE FORMATION OF CUPRAMMONIUM COMPOUNDS

Part III. Composition of Cupric-Ammino Chlorides

BY ARUN K. DEY

(*Chemical Laboratories, University of Allahabad*)

Received on October 7, 1957

ABSTRACT

The existence of tri-, tetra-, penta- and hexa-ammoniates of copper has been inferred from an electrical conductance study of $\text{CuCl}_2-\text{NH}_3$ system.

In previous parts of the series,^{1,2} the systems $\text{CuSO}_4-\text{NH}_3$ and $\text{Cu}(\text{NO}_3)_2-\text{NH}_3$ have been studied in aqueous solution. In other communications on cuprammonium compounds, we have reported the preparation of pent-ammino cupric sulphate,³ existence of hexammino cupric sulphate in solution⁴ and the colloidal nature of cuprammonia solutions.⁵ In this paper the electrical conductivity method of Dey and Bhattacharya⁶ has been employed to the study of the system $\text{CuCl}_2-\text{NH}_3$ in aqueous solution.

EXPERIMENTAL

AnalaR BDH sample of cupric chloride and E. Merck's ammonia solution were employed. Solutions of the reagents were prepared by dissolution in water and standardised by the usual methods. For electrical conductance studies, the method adopted was the same as in the previous parts of the series. The final concentration of cupric chloride was 0.01 M and the temperature of observation 30° C.

Extinction coefficient measurements were not possible in this system, as the solutions were not optically clear and were in many cases colloidal in nature.

RESULTS AND DISCUSSION

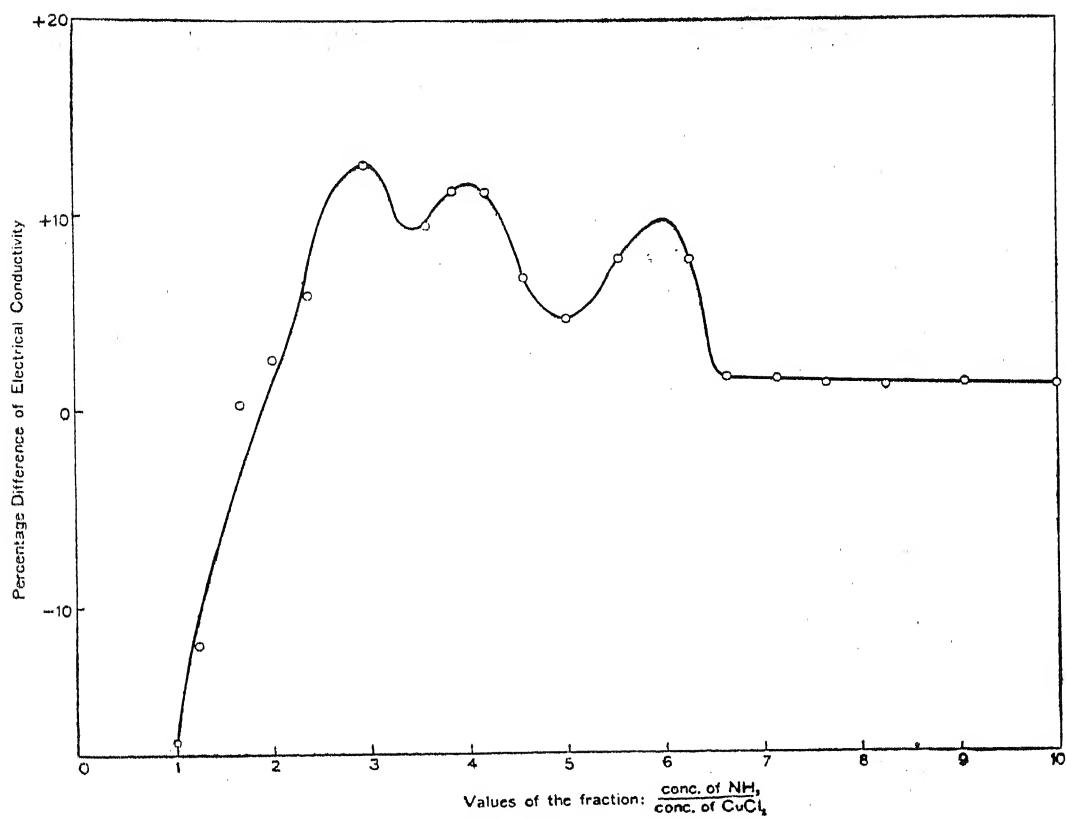
The percentage difference in electrical conductance due to complex formation between cupric chloride and ammonia in solution is shown in Table I.

103

TABLE I
Electrical conductivity of CuCl₂—NH₃ system

Ratio Cu: NH ₃	Sum of the conductance of constituents × 10 ⁴ mhos	Observed conductance of the mixture × 10 ⁴ mhos	Difference × 10 ⁴ mhos	Percentage difference
1: 10.0	21.75	22.01	0.26	1.19
1: 9.09	21.60	21.87	0.27	1.25
1: 8.25	21.56	21.85	0.29	1.34
1: 7.69	21.52	21.84	0.32	1.48
1: 7.14	21.43	21.79	0.36	1.68
1: 6.67	21.42	21.80	0.38	1.78
1: 6.25	21.24	22.87	1.63	7.67
1: 5.55	20.99	22.60	1.61	7.67
1: 5.00	20.87	21.88	1.01	4.84
1: 4.55	20.53	21.96	1.43	6.96
1: 4.17	20.44	22.70	2.26	11.05
1: 3.85	20.30	22.55	2.25	11.08
1: 3.57	20.16	22.03	1.87	9.28
1: 2.94	20.05	22.56	2.51	12.51
1: 2.38	19.87	21.05	1.18	5.95
1: 2.00	19.78	20.28	0.50	2.53
1: 1.67	19.68	19.74	0.06	0.30
1: 1.25	19.56	17.25	-2.31	-11.81
1: 1.00	19.41	16.14	-3.27	-16.84

It is evident from the composition-percentage difference curve (Fig. 1), that sharp breaks occur at 3, 4, 5 and 6 moles of NH₃ per atom of copper, showing the existence of the corresponding complex ions in solution.

FIG 1. Conductometric Study of $\text{CuCl}_2\text{-NH}_3$ System.

REFERENCES

1. DEY, A. K. AND BHATTACHARYA, A. K., 1952, *Z. phys. Chem.*, **200**, 23.
2. ———, 1957, *Proc. Nat. Acad. Sci. (India)*, **26A**, 98.
3. ——— AND BHATTACHARYA, A. K., 1946, *Proc. Ind. Acad. Sci.*, **32 A**, 259.
4. ———, 1946, *Nature*, **158**, 95; 1947, *Ibid.*, **159**, 333.
5. ———, 1948, *J. Colloid Sci.*, **3**, 473.
6. ——— AND BHATTACHARYA, A. K., 1945, *Curr. Sci.*, **14**, 69, 201.

ADSORPTION OF PHOSPHATES BY A CALCAREOUS SAND

BY N. R. DHAR AND S. G. MISRA

(Sheila Dhar Institute of Soil Science, Allahabad University, Allahabad)

Received on August 10, 1957

MANY mechanisms have been proposed to explain phosphate retention by soils and they have been summarized by Wild.¹ They include fixation by iron and aluminium in acid soils either in the form of iron or aluminium phosphate or the adsorption of phosphate ions by the hydrous oxides of iron and aluminium, the precipitation by divalent cations in neutral and alkaline soils; the fixation by clay minerals and bond linkage to the clay lattice through the exchangeable cation. Patel and Viswanath² reported that phosphate fixation increased with an increase in the clay content of soils.

In this paper the adsorption of soluble phosphates of calcium, ammonium and potassium by a calcareous sand was studied with a view to find out the fate of soluble phosphate-fertilizers when applied to the sandy soils of the seacoasts.

EXPERIMENTAL PROCEDURE

42.5 gm. of the calcareous sand collected from the seashores of Madras and of known chemical composition was shaken for 2 hours in glass-stoppered bottles with 100 c.c. of phosphate solutions of 0.01 M, 0.005 M and 0.002 M. The amount of phosphate adsorbed was found out by the differences in the concentration of the phosphate present in the original solution and after the equilibrium was attained after a period of 48 hours. The

RESULTS

TABLE I

Per cent. chemical composition of the calcareous sand passed through 100-mesh sieve (oven-dried)

Loss on ignition	..	1.12	Exchangeable bases m.e./100
HCl-insoluble	..	88.20	Ca 17.4
Sesquioxides	..	2.32	Mg 5.0
Fe ₂ O ₃	..	0.47	K 1.4
CaO	..	5.60	Na 1.2
MgO	..	0.47	
K ₂ O	..	0.99	pH 8.0
P ₂ O ₅	..	0.05	
Na ₂ O	..	0.06	

TABLE II

Adsorption of cations and phosphate from soluble phosphates (12.5 gm. sand + 100 c.c. phosphate solution)

Adsorption of ions from phosphate solution	Concentration			M/500
	M/100	M/200	Adsorption per 100 gm.	
Adsorption per 100 gm.	% adsorbed	% adsorbed per 100 gm.	Adsorption per 100 gm.	% adsorbed
1. Adsorption of H_2PO_4 ions (as P_2O_5) from monocalcium phos- phate ..	0.2302	22.5	0.0467	8.2
2. Adsorption of H_2PO_4 ions (as P_2O_5) from KH_2PO_4 ..	0.0490	8.5	0.0273	9.2
3. Adsorption of HPO_4 ions (as P_2O_5) from K_2HPO_4 ..	0.0262	5.7	0.0136	5.8
4. Adsorption of PO_4 ions (as P_2O_5) from K_3PO_4	0.0647	13.3	0.0520	21.7
5. Adsorption of H_2PO_4 ions (as P_2O_5) from $NH_4H_2PO_4$..	0.0385	6.7	0.0185	6.5
6. Adsorption of HPO_4 ions (as P_2O_5) from $(NH_4)_2HPO_4$..	0.0402	7.1	0.0209	7.1
				0.0009
				0.8

TABLE II—*Contd.*

Adsorption of ions from phosphate solution	Concentration				
	M/100	M/200	M/500	Adsorption per 100 gm.	% adsorbed
7. Adsorption of PO_4 ions (as P_2O_5) from $(\text{NH}_4)_3\text{PO}_4$..	0.0897	13.5	0.0452	13.6	0.0155
<i>a.</i> Adsorption of Ca^{++} as Ca from $\text{CaH}_4(\text{PO}_4)_2$..	0.0680	22.1	(—) 0.0084	..	(—) 0.0128
<i>b.</i> Adsorption of K^+ (as K_2O) from KH_2PO_4 ..	0.0890	19.0	0.0245	13.2	Nil
<i>c.</i> Adsorption of K^+ (as K_2O) from K_2HPO_4 ..	0.0934	14.3	Nil	Nil	Nil
<i>d.</i> Adsorption of K^+ (as K_2O) from K_3PO_4 ..	0.0460	4.8	0.0848	18.2	0.0430
<i>e.</i> Adsorption of NH_4^+ (as NH_4) from $\text{NH}_4\text{H}_2\text{PO}_4$..	0.0129	9.0	Nil	..	21.8
<i>f.</i> Adsorption of NH_4^+ (as NH_4) from $(\text{NH}_4)_2\text{HPO}_4$..	0.0316	11.0	Nil	..	61.4
<i>g.</i> Adsorption of NH_4^+ (as NH_4) from $(\text{NH}_4)_3\text{PO}_4$..	Nil	..	Nil	..	5.0

treated sand was oven-dried and analysed for its exchangeable bases by the normal ammonium acetate method.³ The adsorption of calcium ions as well as ammonium and potassium ions has also been reported. The adsorptions have been calculated per 100 gm. of the sand and the percentage of the adsorbed ions from the original solution has also been given.

TABLE III
Exchangeable bases in the phosphated sand (m.e./100)

Treatment		Ca	Mg	K
$\text{CaH}_4(\text{PO}_4)_2$	M/100	14.7	4.0	1.0
	M/200	13.3	5.0	1.1
	M/500	12.0	5.0	1.2
KH_2PO_4	M/100	8.3	5.0	1.4
	M/200	10.0	5.0	1.4
	M/500	12.1	5.0	1.4
K_2HPO_4	M/100	9.1	5.0	1.2
	M/200	10.7	5.0	2.2
	M/500	10.6	5.0	1.4
K_3PO_4	M/100	14.6	5.0	2.4
	M/200	10.4	4.8	1.4
	M/500	12.3	4.8	1.5
$\text{NH}_4\text{H}_2\text{PO}_4$	M/100	13.0	5.0	1.4
	M/200	12.0	5.0	1.4
	M/500	12.0	5.0	1.4
$(\text{NH}_4)_2\text{HPO}_4$	M/100	8.7	4.1	1.9
	M/200	9.2	5.0	1.4
	M/500	8.6	5.1	1.4
$(\text{NH}_4)_3\text{PO}_4$	M/100	15.0	5.0	1.5
	M/200	18.6	5.0	1.4
	M/500	13.1	5.0	1.4

DISCUSSION

From a perusal of the above tables it is clear that at equimolar concentration the adsorption of phosphate is greatest with monocalcium phosphate. Then comes $(\text{NH}_4)_3\text{PO}_4$ and K_3PO_4 solutions. The per cent. adsorption of phosphate goes on decreasing as the concentration is lowered. In all the cases there is not more than 13-22% of the phosphate adsorbed.

from the original solutions. With ammonium phosphates, the phosphate adsorption goes on increasing as the pH of the phosphate solutions increases from $(\text{NH}_4)_2\text{HPO}_4$ to $(\text{NH}_4)_3\text{PO}_4$, which is alkaline.

The cations are also adsorbed along with the phosphate. Highest amount of K_2O is adsorbed from K_3PO_4 and K_2HPO_4 solutions. Some of the adsorbed potassium is in the exchangeable form as is reflected from an increase in the exchangeable K in the treated sand. However, the adsorption of Ca^{++} , K^+ and NH_4^+ lowers the exchangeable calcium in all the cases. With monocalcium phosphate in spite of the calcium ions being adsorbed, the exchangeable calcium decreases. In other cases, base-exchange by NH_4^+ and K^+ ions may be possible. But the amounts of NH_4^+ and K^+ adsorbed are in no way equivalent to the decrease in the exchangeable calcium content of the sand. The decreases in exchangeable magnesium and potassium are insignificant.

The decrease in exchangeable calcium by phosphate treatment clearly indicates the possibility of combination of exchangeable calcium with the phosphate adsorbed. But the amount of phosphate adsorbed in all cases does not exceed 2-3 m.e. hence the decrease in the exchangeable calcium cannot be explained. The large amount of calcium existing as CaCO_3 in the sea sand and its high pH values are bound to affect the phosphate fixation considerably. Hence it appears that though the phosphates decrease the exchangeable calcium, the actual mechanism of the interaction between the exchangeable calcium and phosphate adsorbed is not clear. It is probable that CaCO_3 , exchangeable calcium and high pH values act together to form some basic phosphate of the carbonato or hydroxy type of phosphate thereby decreasing exchangeable calcium. Such a phenomenon has been suggested by Dhar and Misra¹ to be responsible for the saving of lime by phosphate application to the soils.

The normal soils when treated with phosphate solutions show a similar decrease in exchangeable calcium. It appears therefore that the sands have the inherent properties of the soils. It also explains that sand fraction in soils is also partly responsible for the fixation of phosphates which is observed in the normal soils. Thus the decrease in the exchangeable calcium by phosphate treatment is a common phenomenon with soils and sands.

The sands by such phosphate adsorption, when phosphatic fertilizers are applied to them, can become rich in phosphate. The sea sands may have acquired some phosphate from the sea-water by such adsorption phenomenon as observed in these experiments.

SUMMARY

A calcareous sea sand has been found to fix appreciable amounts of phosphate together with the cations like potassium, calcium and ammonium. A definite decrease in the exchangeable calcium has been observed after phosphate treatment to the sand. This property is common to the normal soils and hence this sand resembles the normal soils in its behaviour towards adsorption of phosphate. Not only the clay fraction but sandy portion of the normal soils is responsible for the observed phosphate fixation in soils. The phosphate treatment may decrease the losses of calcium by leaching from such sands.

REFERENCES

1. WILD, A., 1949, *Jour. Soil Sci.*, **1**, 221-35.
2. PATEL, D. K. AND VISWANATH, B., 1946, *Indian Jour. Agr. Sci.*, **15** (5), 428-34.
3. KELLEY, W. P., *Cation Exchange in Soils*, p. 99.
4. DHAR, N. R. AND MISRA, S. G., 1955, *Nat. Acad. Sci. India*, **24** (3).

CHARACTERISATION OF THE GAMMA FUNCTION

By D. P. BANERJEE

(*Department of Mathematics, Meerut College, Meerut, U.P., India*)

Received on August 12, 1957

LUKACS (1955) AND LAHA (1954) considered the Characterisation of the Gamma distribution.

Here I shall consider similar but different problem.

The distribution function, of Gamma distribution, is denoted by

$$F(x, a, \lambda) = \frac{a^\lambda}{\Gamma(a)} \int_0^x t^{\lambda-1} e^{-at} dt \text{ if } x > 0 \text{ and } 0 \text{ if } x \leq 0.$$

The characteristic function of the distribution of the Gamma function is

$$\left(1 - \frac{it}{a}\right)^{-\lambda}$$

THEOREM 1. If x, y are independent Gamma variates with parameters 1 and m respectively,

then $u = x + y$, $v = \frac{x-y}{x+y}$ are independent variates.

The joint distribution function of x, y is

$$f(x, y) = \frac{1}{\Gamma(1)m} e^{-(x+y)} x^{m-1} y^{m-1}$$

where

$$0 \leq x \leq a, \quad 0 \leq y \leq a.$$

Now

$$u = x + y, \quad x - y = nv.$$

Hence

$$x = \frac{u(1+v)}{2}, \quad y = \frac{u(1-v)}{2},$$

Hence the joint distribution function of

$$u, v \text{ is } g(u, v) = \frac{1}{2\Gamma(l)m} e^{-u} u^{l+m-1} \left(\frac{1+v}{2}\right)^{l-1} \left(\frac{1-v}{2}\right)^{m-1}$$

$$0 \leq u \leq a, -1 \leq v \leq 1.$$

Hence u, v are independent.

THEOREM 2. Let x, y be two non-degenerate and positive random variables which are independently distributed. The random variables

$$u = x + y \text{ and } v = \frac{x - y}{x + y}$$

are independently distributed if both x, y have Gamma distribution with the same scale parameter and

$$|E(u)| < 1, |E(v)| < 1 \text{ and } E(v^2) - \{E(v)\}^2 \geq 0.$$

Since v is bounded, all the moments of the distribution of v exist.

Let

$$\theta_1 = E(v) = E\left(\frac{x - y}{x + y}\right)$$

and

$$\theta_2 = E(v^2) = E\left(\frac{x - y}{x + y}\right)^2$$

Then

$$\theta_2 - \theta_1^2 \geq 0 \text{ and } |\theta_1| < 1, |\theta_2| < 1$$

by hypothesis.

Let

$$f(t_1) = \int_0^\infty e^{it_1 x} dF(x) \text{ for } \operatorname{Im}(t_1) > 0$$

and

$$g(t_1) = \int_0^\infty e^{it_1 y} dG(y) \text{ for } \operatorname{Im}(t_1) > 0.$$

Since

$x + y, \frac{x - y}{x + y}$ are independent

$$\begin{aligned} & \mathbb{E} \left\{ e^{it_1(x+y)+it_2 \left(\frac{x-y}{x+y} \right)} \right\} \\ &= \mathbb{E} \{ e^{it_1(x+y)} \} \cdot \mathbb{E} \left\{ e^{it_2 \left(\frac{x-y}{x+y} \right)} \right\}. \end{aligned}$$

Hence

$$\begin{aligned} & \int_0^\infty \int_0^\infty e^{it_1(x+y)+it_2 \left(\frac{x-y}{x+y} \right)} dF(x) dG(y) \\ &= \int_0^\infty \int_0^\infty e^{it_1(x+y)} dF(x) dG(y) \int_0^\infty \int_0^\infty e^{it_2 \left(\frac{x-y}{x+y} \right)} dF(x) dG(y). \end{aligned}$$

Differentiating both the sides with respect to t_1 and then with respect to t_2 and putting $t_2 = 0$ we have

$$\begin{aligned} & \int_0^\infty \int_0^\infty (x-y) e^{it_1(x+y)} dF(x) dG(y) \\ &= \theta_1 \int_0^\infty \int_0^\infty (x+y) e^{it_1(x+y)} dF(x) dG(y) \end{aligned}$$

where

$$\theta_1 = \int_0^\infty \int_0^\infty \frac{x-y}{x+y} dF(x) dG(y).$$

Hence

$$(1 - \theta_1) \frac{f'(t)}{f(t)} = (1 + \theta_1) \frac{g'(t)}{g(t)} \quad (3)$$

Hence

$$\{f(t_1)\}^{1-\theta_1} = \{g(t_1)\}^{1+\theta_1}$$

since

$$f(0) = g(0) = 1.$$

Differentiating (1) twice with respect to t_1 and then with respect to t_2 and putting $t_2 = 0$

we have

$$\begin{aligned} & \int_0^\infty \int_0^\infty (x-y)^2 e^{it_1(x+y)} dF(x) dG(y) \\ &= \theta_2 \int_0^\infty \int_0^\infty (x+y)^2 e^{it_1(x+y)} dF(x) dG(y). \end{aligned}$$

Hence

$$(1 - \theta_2) \frac{f''(t)}{f(t)} = 2(1 + \theta_2) \frac{f'(t)g'(t)}{f(t)g(t)} - (1 - \theta_2) \frac{g''(t)}{g(t)}.$$

Let

$$\frac{f'(t)}{f(t)} = \phi(t), \quad \frac{g'(t)}{g(t)} = \psi(t)$$

Then

$$\frac{f''(t)}{f(t)} = \phi^1(t) + \phi^2(t) \quad \text{and} \quad \frac{g''(t)}{g(t)} = \psi^1(t) + \psi^2(t).$$

Again by (2),

$$(1 - \theta_1) \phi = (1 + \theta_1) \psi.$$

Hence

$$(1 - \theta_1) \phi^1 = (1 + \theta_1) \psi^1.$$

Hence

$$\phi^1(t) = \frac{\phi^2(b)}{\rho}.$$

Where

$$\rho = \frac{(1 - \theta_2)(1 + \theta_1)}{\theta_2 - \theta_1^2} > 0 \quad \text{If} \quad \theta_2 - \theta_1^2 \neq 0$$

we have

$$\frac{d\phi(t)}{\phi^2(t)} = \frac{dt}{\rho} \quad \text{or} \quad \frac{1}{\phi(t)} = A - \frac{t}{\rho}.$$

Hence

$$\frac{f'(t)}{f(t)} = \phi(t) = \frac{1}{A - \frac{t}{\rho}}.$$

Hence

$$f(t) = \frac{B}{\left(A - \frac{t}{\rho}\right)^\rho}.$$

Now

$$f(0) = 1, f'(0) = ik_1.$$

Hence

$$A = \frac{1}{iK_1}, \quad B = \left(\frac{1}{iK_1}\right)^\rho.$$

Hence

$$f(t) = \frac{1}{\left(1 - \frac{it}{a}\right)^\rho}.$$

Where

$$a = \frac{\rho}{K_1}$$

Then by (3)

$$\begin{aligned} g(t) &= [f(t)] \frac{1 - \theta_1}{1 + \theta_1} \\ &= \frac{1}{\left[1 - \frac{it}{a}\right] \frac{1 - \theta_1}{1 + \theta_1} \rho} \quad \text{for } \operatorname{im} t > 0. \end{aligned}$$

Hence x, y are Gamma variates with the same scale parameter.

If $\theta_2 = \theta_1^2$ then $\phi^1(t) = 0$ the variables will have degenerate distribution. Hence we have the theorem.

REFERENCES

LAHA, R. G., 1954, *Ann. Math. Stat.*, **25**, 784-87.

LUKACS, ENGENE, 1955, *ibid.*, **26**, 319-24.

SOME RELATIONS BETWEEN SPECIAL FUNCTIONS

BY B. B. MISRA

(*D. S. B. Government College, Naini Tal*)

Received on January 1, 1957

§ 1. INTRODUCTION

DEVERALL AND THORNE [1] have used the methods of Operational Calculus to discover some new relations involving special functions. The object of this note is to obtain some more such relations.

Following Mc Lachlan and Humbert (1950), we shall call $f(p)$ to be the Laplace Transform of $\phi(t)$, if

$$f(p) = p \int_0^\infty e^{-pt} \phi(t) dt$$

and shall write this as

$$f(p) \doteq \phi(t).$$

§ 2

If in the identity

$$(x+y)^n = \sum_{r=0}^n \binom{n}{r} (x-y)^{n-r} (2y)^r \quad (A)$$

we put $x = 1/p$, $y = 1$, we have

$$\left(1 + \frac{1}{p}\right)^n = \sum_{r=0}^n \binom{n}{r} 2^r \left(\frac{1}{p} - 1\right)^{n-r}$$

which can be written as

$$\sum_{r=0}^n \binom{n}{r} \left(\frac{1}{p}\right)^r = \sum_{r=0}^n \binom{n}{r} 2^r \left(\frac{1}{p} - 1\right)^{n-r} \quad (B)$$

Now the inverse Laplace Transform of $(1/p)^r$ is $\frac{t^r}{\Gamma(r+1)}$

and that of

$$(1/p - 1)^{n-r}$$

is

$$(-1)^{n-r} L_{n-r}(t) [2];$$

thus, interpreting term by term, we get

$$\sum_{r=0}^n \binom{n}{r} \frac{t^r}{\Gamma(r+1)} = \sum_{r=0}^n \binom{n}{r} (-1)^{n-r} 2^r L_{n-r}(t) \quad (1)$$

where $L_n(t)$ is Laguerre's Polynomial.

If we multiply both sides of (B) by $1/\sqrt{p}$ we have

$$\sum_{r=0}^n \binom{n}{r} \frac{1}{p^{r+\frac{1}{2}}} = \sum_{r=0}^n \binom{n}{r} 2^r \frac{1}{\sqrt{p}} \left(\frac{1}{p} - 1\right)^{n-r}$$

and the inverse Laplace Transform of $(1/\sqrt{p})(1/p - 1)^n$ is

$$\frac{2^{n+\frac{1}{2}}}{\sqrt{\pi}} \frac{|n|}{[2n+1]} e^{t/2} D_{2n+1}(\sqrt{2t}) \quad [3];$$

thus, interpreting term by term, we get

$$\begin{aligned} \sum_{r=0}^n \binom{n}{r} \frac{t^{r+\frac{1}{2}}}{\Gamma(r+\frac{3}{2})} &= \sum_{r=0}^n \binom{n}{r} \frac{|n-r|}{[2n-2r+1]} \\ &\times \frac{2^{n+\frac{1}{2}}}{\sqrt{\pi}} e^{t/2} D_{2n-2r+1}(\sqrt{2t}) \end{aligned} \quad (2)$$

where $D_n(t)$ is the parabolic cylinder function.

§ 3

Again if we put $x = 1$, $y = 1/p$ in the identity

$$\sum_{r=0}^n \binom{n}{r} x^{n-r} y^r = \sum_{r=0}^n \binom{n}{r} (x-y)^{n-r} (2y)^r$$

we get

$$\sum_{r=0}^n \binom{n}{r} \frac{1}{p^r} = \sum_{r=0}^n \binom{n}{r} \left(1 - \frac{1}{p}\right)^{n-r} 2^r p^{-r}.$$

Now the inverse Laplace Transform of $p^{-r} (1 - 1/p)^{n-r}$ is

$$\frac{(-1)^{r-n}}{\Gamma(n+1)} t^{(r-1)/2} e^{t/2} W_{n-r/2+\frac{1}{2}, r/2}(t) [4];$$

thus term by term interpretation gives

$$\sum_{r=0}^n \binom{n}{r} \frac{t^r}{\Gamma(r+1)} = \frac{1}{\Gamma(n+1)} \sum_{r=0}^n \binom{n}{r} (-1)^{r-n} 2^r t^{(r-1)/2} \\ \times e^{t/2} W_{n-r/2+\frac{1}{2}, r/2}(t) \quad (3)$$

where $W_{k, m}$ is the Whittaker function.

From (1) and (3), we obtain the following relation between Laguerre's Polynomial and Whittaker function :

$$\sum_{r=0}^n \binom{n}{r} (-1)^{n-r} 2^r L_{n-r}(t) \\ = \frac{1}{\Gamma(n+1)} \sum_{r=0}^n \binom{n}{r} (-1)^{r-n} 2^r t^{\frac{1}{2}(r-1)} e^{t/2} W_{n-r/2+\frac{1}{2}, r/2}(t) \quad (4)$$

My thanks are due to Dr. K. M. Saksena for his suggestions.

REFERENCES

1. DEVERALL, L. I AND THORNE, C. J., 1952, *Mathematics Magazine*, **25**, 183-87.
2. MC LACHLAN, N. W. AND HUMBERT, P., 1950, *Formulaire pour le Calcul symbolique*, p. 56.
3. —————, *ibid.*, p. 52.
4. —————, *ibid.*, p. 51.

BEHAVIOUR OF ALKALI SOILS IN FIXING MONOCALCIUM PHOSPHATE FROM SOLUTIONS

By N. R. DHAR AND S. G. MISRA

(*Sheila Dhar Institute of Soil Science, University of Allahabad, Allahabad*)

Received August 10, 1957

THERE are conflicting views regarding the fixation of superphosphate when it is added to the soils. The calcium carbonate content, the sesquioxides, high pH values, the exchangeable bases and the amount of fine particles have been attributed as the principal participants in fixing phosphates. Ravikovitch¹ for the first time proposed the phosphate fixation to be a H_2PO_4 -Ca-clay linkage which was supported by Scarseth² and Allison.³ Ellis and Troug⁴ opposed this linkage theory on the basis that magnesium soils behaved differently. Wey⁵ proposed a link between the peripheral aluminium in the octahedral layer of montmorillonite and H_2PO_4 ions from the soil or phosphoric acid. Damaty and Axley⁶ proposed a H_2PO_4 -Ca-Soil linkage.

The present investigations were carried on with a view to find out the adsorption of calcium and phosphate ions from monocalcium phosphate solutions when added to *Usar* (alkali) soils.

EXPERIMENTAL PROCEDURE

The *Usar* soil samples used in adsorption experiments were designated as U, 36, 33, N/1 and A/2. The first sample was collected from alkali land of Soraon, near Allahabad whilst the others were brought from a sugar factory farm at Faizabad (U.P.). The chemical compositions of these soils is given in Table I.

12.5 gm. of the oven-dried samples, previously passed through 100-mesh sieve, were used for fixation or adsorption experiments. 100 c.c. of M/100, M/200 and M/500 solutions of monocalcium phosphate were used. The soils were shaken with phosphate solution in glass-stoppered bottles for two hours and filtered after 24 hours. The filtrates were analysed for their phosphate contents and adsorbed phosphate was found out by the difference in the original and the equilibrium concentrations of phosphate solutions. Adsorption of calcium was also found out similarly. In the case of sample U, three successive adsorptions were determined. The treated soils were very carefully transferred to the bottles and 100 c.c. of different concentrations of phosphate solution were added and the adsorption was found out.

The treated samples were oven-dried and analysed for their exchangeable bases. Besides the sample U, adsorption with other soils was found only with one concentration of phosphate solution and exchangeable calcium was determined in the phosphated samples. The exchangeable calcium was determined by the well-known normal ammonium acetate method and phosphate by phospho-molybdate precipitation method. The adsorption has been reported as P_2O_5 adsorbed per 100 gm. of the soils used. The percentage of the adsorbed ions from the original solution has also been included.

RESULTS

TABLE I
Chemical composition of the soils used

No. of the soils	Constituents %					
	SiO ₂	R ₂ O ₃	CaO	MgO	K ₂ O	P ₂ O ₅
U	81.00	11.29	0.980	1.810	0.843	0.0914
36	85.60	8.37	0.397	1.171	2.050	0.0623
33	87.70	7.35	0.459	0.996	2.183	0.0599
N-1	84.80	8.52	0.308	1.210	1.813	0.0747
A-2	84.00	8.60	0.620	1.410	1.941	0.0528

TABLE II
Repeated adsorption of calcium and phosphate ions from monocalcium phosphate solution by Usar soil (U)

Constituents adsorbed in successive adsorptions	Concentration of monocalcium phosphate					
	M/100		M/200		M/500	
	Adsorption per 100 gm.	% adsorbed	Adsorption per 100 gm.	% adsorbed	Adsorption per 100 gm.	% adsorbed
P_2O_5	0.4060	35.9	0.1437	25.3	0.0188	8.3
	0.1563	13.8	0.0861	15.2	0.0113	5.3
	0.1045	9.2	0.0452	7.9	0.0512	22.6
Ca	(1) 0.2855	92.4	0.1440	93.3	0.0618	100.0
	(2) 0.1145	37.0	0.0844	54.6	0.0492	79.7

TABLE III
Exchangeable bases of the treated soil—U (m.e./100)

Originally present	After treating with phosphate solution		
	M/100	M/200	M/500
Ca	14.1	25.0	21.3
Mg	4.6	3.0	3.2
K	1.8	1.6	1.6
Na	2.4	0.0	0.2

TABLE IV
Adsorption of calcium and phosphate ions from M/100 monocalcium phosphate solution by samples 36, 33, N/1 and A/2

No. of the soils	Adsorption of H_2PO_4 ions		Adsorption of Ca ions	
	Adsorption per 100 gm.	% adsorbed	Adsorption per 100 gm.	% adsorbed
36	0.2880	26.2	0.1440	45.0
33	0.3353	30.6	0.1760	55.0
N/1	0.3434	31.4	0.1337	41.8
A/2	0.4257	38.9	0.2080	65.0

TABLE IV A
Adsorption of calcium and phosphate from M/100 monocalcium phosphate solution by normal soils (S_1, S_2, S_3) and bentonites (B_1, B_2, B_3)

(5 gm. bentonites and 12.5 gm. soils \pm 100 c.c. solution)

Reference No.	Adsorption of H_2PO_4 ions		Adsorption of Ca ions	
	Adsorption per 100 gm.	% adsorbed	Adsorption per 100 gm.	% adsorbed
S_1	0.3240	31.6	0.1250	40.9
S_2	0.4096	40.0	0.1454	47.6
S_3	0.3552	34.6	0.1470	48.1
B_1	0.5644	20.0	0.7162	93.7
B_2	0.5838	20.7	0.6960	91.6
B_3	1.1950	42.3	0.4142	55.0

TABLE V

Exchangeable calcium and pH values of treated samples with M/100 monocalcium phosphate solution

No. of soils	Original pH values	After phosphate adsorption, pH values	Exchangeable calcium (m.e./100)	
			Originally	After phosphate adsorption
U	10.3	7.9	14.1	20.1
36	8.6	6.8	9.5	15.7
33	9.4	7.0	10.4	17.6
N/1	8.1	6.6	5.0	13.3
A/2	9.4	7.0	13.0	22.5

DISCUSSION

From the foregoing results it is clear that the *Usar* soil, U, goes on adsorbing phosphate and calcium ions from monocalcium phosphate solution but the amounts so adsorbed go on decreasing. The percentage of P_2O_5 adsorbed from the original phosphate solution in the first adsorption is 35.9 whilst much greater percentage of calcium is being adsorbed simultaneously. As the concentration of phosphate solution is decreased the percentage adsorption as well as the per cent. adsorbed portion goes on decreasing in the case of phosphate whilst calcium shows a different behaviour. Practically all the calcium ions are adsorbed from three different concentrations of monocalcium phosphate in the first adsorption and the amounts adsorbed in the successive adsorptions are also considerable. Thus there is a preferential adsorption of calcium ions by the *Usar* soil, U, over the phosphate ions. A similar behaviour has been observed by us in bentonites as well but the phosphate adsorbed by them is also high (*vide* Table IV A). The amount of phosphate adsorbed by normal soils, having pH values from 7.3 to 7.6, has been found to be equal to the phosphate adsorbed by this particular *Usar* soil. But the amount of calcium adsorbed by normal soils at higher dilutions is negligible whilst at lower dilutions the adsorption of calcium is only half or less to that of *Usar* soil, U. Other *Usar* soils reported

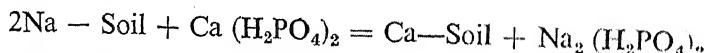
in Table IV show a similar adsorption of phosphate and lesser adsorption of calcium.

The *Usar* soils are deficient in CaO and P₂O₅ contents but have higher MgO and K₂O contents. The high MgO and K₂O contents together with high pH values are responsible for phosphate fixation because on adding monocalcium phosphate to an alkali soil dicalcium phosphate and tricalcium phosphates which are very sparingly soluble in water are formed at high pH values. Also, insoluble dimagnesium and trimagnesium phosphates may be formed. The low percentages of CaO and P₂O₅ in alkali soils seem to be partly responsible for the adsorption of calcium and phosphate ions. The *Usar* soils contain soluble Na₂CO₃ which precipitates out calcium as CaCO₃ from monocalcium phosphate and also helps in decreasing the phosphate adsorption by the production of soluble sodium phosphates. The probable reactions are:—

1. $\text{Ca}(\text{H}_2\text{PO}_4)_2 + \text{OH}' \rightleftharpoons \text{CaHPO}_4 + \text{H}_3\text{PO}_4 + \text{H}_2\text{O}$
2. $\text{Ca}(\text{H}_2\text{PO}_4)_2 + \text{Na}_2\text{CO}_3 \rightleftharpoons \text{CaCO}_3 + \text{Na}_2(\text{H}_2\text{PO}_4)_2$
3. $\text{Ca}(\text{H}_2\text{PO}_4)_2 + \text{MgO} \text{ or } \text{CaO} \rightleftharpoons 2 \text{CaHPO}_4 + \text{H}_2\text{O}$.

The above reactions explain lower phosphate adsorption by *Usar* soils because of the presence of sodium carbonate which is absent in normal soils. The bentonites show a marked phosphate adsorption because they are very well supplied with exchangeable calcium and magnesium. The *Usar* soils used in these experiments are not rich in total or exchangeable calcium.

A most notable feature of the present investigations is an increase in the exchangeable calcium content of the phosphated *Usar* soils. It has been observed by us that all the normal soils show a definite decrease in their exchangeable calcium status after phosphate adsorption from monocalcium phosphate. The bentonites have been found to resemble the *Usar* soils. An increase in the exchangeable calcium can be envisaged in *Usar* soils according to the following equation:—



In most of the cases all the adsorbed calcium is wholly in the exchangeable form; hence the possibility of the formation of CaCO₃ and CaHPO₄ seems small but as both of these compounds are slightly soluble in ammonium acetate solution, the possibility of their formation cannot be totally ignored. However, the increase in exchangeable calcium varies from 5 to 11 m.e./100 whilst exchangeable Na does not exceed 2.4 m.e. in any case. Hence besides exchange with Na ions, calcium ions are also held in the exchangeable state

by the clay minerals present in *Usar* soils. A considerable decrease in the pH values of the treated soils shows that the sodium ions from the exchange-complex have been replaced by calcium ions. The soils became normal and hence the treatment of monocalcium phosphate to alkali soils may be used to reclaim them. The soils become rich in exchangeable calcium. The *Usar* soils may also contain montmorillonite so as to resemble the adsorption shown by bentonites and also to explain the excess of calcium held by the soil in exchangeable form.

SUMMARY

The *Usar* soils adsorb both calcium and phosphate ions from monocalcium phosphate solutions but there is a preferential adsorption of calcium ions over the phosphate ions. The adsorption of phosphate ions by *Usar* soils is smaller than by normal soils or bentonites. An increase in the exchangeable calcium after treatment very clearly shows an exchange reaction between the sodium ions of the soil-exchange-complex and the calcium of the solution. The sodium carbonate present in alkali soils diminishes the phosphate adsorption due to its reaction on calcium phosphates forming sodium phosphates. The *Usar* soils after adsorbing phosphate and calcium ions attain lower pH values and hence the application of monocalcium phosphate can be used to reclaim *Usar* soils.

REFERENCES

1. RAVIKOVITCH, S., 1934, *Soil Sci.*, **38**, 279-90.
2. SCARSETH, G. D., 1935, *Jour. Amer. Soc. Agr.*, **27**, 596-616.
3. ALLISON, L. E., 1943, *Soil Sci.*, **55**, 333-42.
4. ELLIS, R. AND TROUG, E., 1956, *Soil Sci. Amer. Proc.*, **19**, 451-57.
5. WEY, R., 1954, *C.R. Acad. Sci., Paris*, **238**, 389-94.
6. DAMATY, H. AND AXLEY, J. H., 1954, *Soil Sci.*, **77**, 453-61.

PHYSICO-CHEMICAL STUDIES IN THE FORMATION OF COMPLEX STANNIOXALATES

Part V. Spectroscopic Study of the System : $\text{SnCl}_4\text{-K}_2\text{C}_2\text{O}_4$

BY ARUN K. DEY

(*Chemical Laboratories, University of Allahabad*)

Received on October 7, 1957

ABSTRACT

Ultra-violet absorption spectra of mixtures of stannic chloride and potassium oxalate solutions have been studied. It has been concluded that the compounds formed are $\text{Sn}(\text{C}_2\text{O}_4)_2$ and $\text{K}_4[\text{Sn}(\text{C}_2\text{O}_4)_4]$. The structures of the compounds have been given and it has been suggested that the first compound involves sp^3 hybrid bonds, while the second sp^3d^4 bonds.

In several communications from these laboratories, the formation of anionic complexes of tetrapositive tin with oxalates, malonates, succinates and tartrates¹⁻³ have been described. In the previous parts of the series⁴⁻⁷ we have described the formation of complex stannioxalates by physico-chemical methods. It has been emphasized that methods involving isolation and subsequent chemical analysis often fail to convey a true picture of the complex ions and it has been recommended that physico-chemical studies in solution must be done to elucidate the composition of complex ions.⁸

This paper records our results on the study of the system $\text{SnCl}_4\text{-K}_2\text{C}_2\text{O}_4$ in aqueous solution, by ultra-violet absorption spectra.

EXPERIMENTAL

A solution of stannic chloride crystals (Schuchardt sample) was dissolved in dilute hydrochloric acid (E. Merck sample) of known concentration. Tin was estimated gravimetrically and the solution diluted and further hydrochloric acid added to get an exact solution of decimolar stannic chloride in normal hydrochloric acid. Solutions of potassium oxalate (BDII AnalaR) of known concentrations were also prepared. Mixtures using the monovariant method, *i.e.*, by adding varying amounts of oxalate to a fixed quantity of stannic chloride solution, were prepared.

For the study of absorption spectra, Adam Hilger Constant Deviation Quartz Spectrograph was used, with copper arc as the source. Different thicknesses of the solutions were used in a Baly's tube. The photographs were taken on Ilford Empress plates. The experiments were carried out at 25° C.

RESULTS AND DISCUSSION

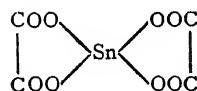
From the plates, the thicknesses of the solutions required for producing absorption up to 2618 Å.U. were read. The values are shown in Table I.

TABLE I

Ratio Sn ^{IV} : C ₂ O ₄ ²⁻	Thickness of solution mm.
1: 0	18 - 16
1: 0.25	18 - 16
1: 0.50	18 - 10
1: 1.00	12 - 10
1: 1.25	10
1: 2.00	5.4
1: 2.50	5.4
1: 2.86	4
1: 3.33	3
1: 4.00	3
1: 4.44	2
1: 5.00	2
1: ∞	2

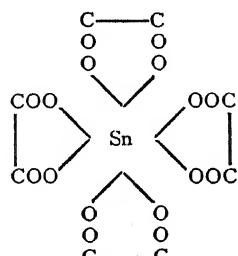
The graph between composition and the required thickness (Fig. 1) shows breaks corresponding to 2 and 4 oxalate per atom of tin, showing the presence of the corresponding compounds. These results are in agreement with those obtained by electrical conductance method, as reported earlier.

The structure of Sn(C₂O₄)₂ may be represented by:



I. Stannic oxalate

The complex ion [Sn(C₂O₄)₄]⁴⁻ has the following structure:—



II. Stannioxalate ion

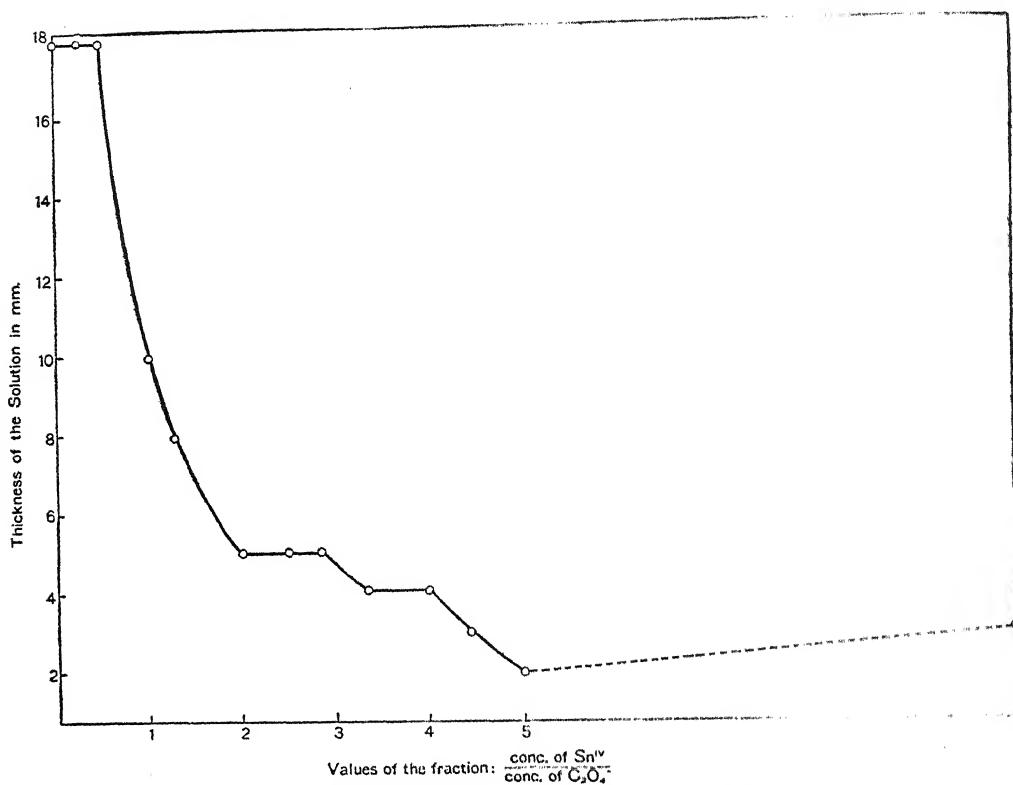


FIG. 1. Absorption spectra of the system $\text{SnCl}_4\text{-K}_2\text{C}_2\text{O}_4$.

In compound (I) the bond is of sp^3 hybrid type, the co-ordination number being four. In the ion (II), the co-ordination number is eight, which is uncommon, but known in the case of oxalate-complexes.⁹ The ion seems to involve sp^3d^4 hybrid bonds.

REFERENCES

1. DEY, A. K., 1946, *University of Allahabad Studies*, **22**, 7.
2. —— AND BHATTACHARYA, A. K., 1945, *Curr. Sci.*, **14**, 69.
3. ——, 1946, *Proc. Nat. Acad. Sci. (India)*, **15 A**, 86.
4. DEY, A. K., 1947, *ibid.*, **16 A**, 27.
5. —— AND BHATTACHARYA, A. K., 1948, *J. Ind. Chem. Soc.*, **25**, 571.
6. ——, 1949, *Proc. Nat. Acad. Sci. (India)*, **18 A**, 121.
7. DEY, A. K., 1950, *ibid.*, **19 A**, 141.
8. —— AND GHOSH, S., 1950, *ibid.*, **19 A**, 158.
9. DEY, A. K., 1948, *J. Colloid Sci.*, **3**, 473.
10. MARCHI, L. E., FERNELIUS, W. C. AND MCREYNOLDS, J. P., 1943, *J. Amer. Chem. Soc.*, **65**, 329.
11. —— AND MCREYNOLDS, J. P., 1943, *ibid.*, **65**, 333.
12. MARCHI, L. E., 1943, *ibid.*, **65**, 2257.

POTENTIOMETRIC DETERMINATION OF AROMATIC AMINES BY THE DIAZO REACTION

BY G. SITARAMAIAH AND R. S. SHARMA
(*Birla College, Pilani*)

Received on August 17, 1957

ABSTRACT

A simple method of estimating aromatic primary amines by potentiometric titration with sodium nitrite is reported. An aliquot (25 ml.) of amine solution of strength about M/4 can be accurately titrated with sodium nitrite solution of ten-fold concentration, in presence of about 8 gm. of concentrated hydrochloric acid, using platinum and saturated calomel electrodes as +ve and -ve electrodes respectively. The titration is always to be carried out below 20° C. The average inflection potential in these titrations has always been found to be 0.585 volts, irrespective of the amine. The error under these conditions shall not exceed $\pm 0.2\%$.

INTRODUCTION

In the estimation of aromatic primary amines by the diazo reaction, using starch-iodide as external indicator, the end-point detection becomes difficult due to lack of sharpness. In dilute solutions a poorer end-point results, and in the case of concentrated solutions the loss of nitrous acid is high. To avoid this difficulty in the detection of end-point in the visual titration method, Muller and Daschelt¹ investigated the possibility of applying the potentiometric method for detecting the end-point of the titration. According to them there is a jump in potential at the equivalence point of the titration of the acid solution of an aromatic primary amine with sodium nitrite, using Pt and saturated calomel electrodes as +ve and -ve electrodes respectively. The titrations were all carried out in highly concentrated solutions. Kolthoff² attempted to apply the reaction in the titration of dilute solutions without success. However the influence of the acid concentration on the inflection potential was not investigated. Hence the present investigation was undertaken to fix the optimum conditions of concentration of amine acid concentration, and temperature. The study was however confined to aniline and *p*-toluidine. Salient points of the investigation were already reported.³

EXPERIMENTAL

1. Apparatus

Potential measurements were all made with a Cambridge Vernier Potentiometer and the null-point was detected by a ballistic galvanometer with lamp and scale arrangement. The titration cell consisted of the same Muller¹ electrodes; a microburette and an ordinary glass stirrer were used in all the titrations.

2. Solutions

Solutions of aniline of different concentrations were made from freshly distilled aniline, by dissolving corresponding amounts of aniline in 30 ml. of hydrochloric acid (Specific gravity 1.16) and making up of the solution to one litre. Standard solutions of *p*-toluidine were made in a similar manner using *p*-toluidine recrystallised from hot dilute alcohol.

Solutions of sodium nitrite were standardised by adding aliquots to a definite volume of standard potassium permanganate solution and titrating the excess of permanganate with standard solution of sodium oxalate. Hydro-

TABLE I
Influence of aniline concentration

Temperature 19° C.; Hydrochloric acid (Sp. gr. 1.16) present in 25 ml. = 7.155 gm.

Strength of aniline solution in Molarity	in gm./litre	Aniline by experiment gm./litre	Percentage error
0.0645	6.377	6.235	0.7
0.1075	11.181	11.117	0.6
0.1613	14.364	14.392	0.2
0.2150	20.510	20.510	0.0
0.3225	30.730	30.700	0.1
0.5376	50.643	50.752	0.2
0.6850	60.527	60.688	0.3
0.8600	80.191	80.487	0.4

chloric acid of specific gravity 1.16 was used in all the experiments. All chemicals used were of A.R. (B.D.H. or Merck) quality.

3. Factors investigated

(a) *Influence of concentration of amine.*—Solutions of aniline and *p*-toluidine of concentrations ranging from M/100 to M/1 were prepared and titrated with standard sodium nitrite solution of about ten-fold concentration. The concentration of hydrochloric acid was kept constant. The temperature throughout these experiments was maintained at 19° C.

(b) *Influence of temperature.*—The influence of temperature was studied up to 40° C. The concentration of the amine solution was kept constant at M/5. The concentration of hydrochloric acid was the same as in factor (a).

(c) *Influence of concentration of hydrochloric acid.*—The influence of the addition of different amounts of hydrochloric acid on the inflection potential was investigated. The concentrations of the amine and temperature were kept constant in all the experiments.

TABLE II

Influence of p-toluidine concentration

Temperature 19° C.; Hydrochloric acid present in 25 ml. = 7.155 gm.

Strength of <i>p</i> -toluidine in Molarity	in gm./litre	<i>p</i> -Toluidine by experiment gm./litre	Percentage error
0.0330	3.529	3.555	0.72
0.0573	6.132	6.095	0.60
0.095	10.164	10.215	0.51
0.140	14.974	14.942	0.21
0.190	20.377	20.335	0.20
0.231	25.312	25.330	0.07
0.280	30.418	30.387	0.10
0.380	36.983	36.941	0.12
0.570	58.223	58.136	0.15

TABLE III

Influence of temperature (Aniline)

Hydrochloric acid in 25 ml. = 7.155 gm.

Temperature °C.	Aniline taken (gm./litre)	Aniline by experiment (gm./litre)	Percentage error
40	21.838	21.667	0.85
30	21.014	21.009	0.56
25	20.862	20.926	0.30
20	20.510	20.510	0.00
15	20.862	20.853	0.04
10	20.862	20.853	0.04

TABLE IV

Influence of temperature (p-Toluidine)

Hydrochloric acid in 25 ml. = 7.155 gm.

Temperature °C.	p-Toluidine taken (gm./litre)	p-Toluidine by experiment (gm./litre)	Percentage error
40	24.922	25.173	1.00
30	24.922	25.062	0.54
25	24.922	24.021	0.37
20	25.312	25.330	0.07
15	24.927	24.951	0.09
10	24.927	24.951	0.09

CONCLUSIONS

As seen from Table I, it is clear that the percentage error is high in the case of very dilute or very concentrated solutions of aniline. Solutions of

TABLE V
Influence of acid concentration

Concentration of aniline = 0.230 M; *p*-toluidine = 0.235 M; Temperature = 19° C.

Sl. No.	Amount of hydrochloric acid present in 25 ml. of amine solution (gm.)	Inflection in potential at equivalence point	
		Aniline mv.	<i>p</i> -Toluidine mv.
1	2.915	35	39
2	4.935	65	46
3	7.155	79	85
4	9.275	82	86
5	11.395	87	90

aniline between 0.2150-0.3225 M gave accurate results, the error in these cases being $\pm 0.1\%$. Muller and Daschelt¹ however used aniline solutions of strength 0.6-0.7 M. In the case of *p*-toluidine as evident from Table II, solutions of strength 0.23-0.38 M gave accurate results. From Table V it is noted that 8-10 gm. of hydrochloric acid shall be present in 25 ml. of amine solution to obtain the maximum jump in potential at the equivalence point. These titrations do not give good results above 20° C., as observed from Tables III and IV, as at higher temperatures the diazonium salt decomposes to give the phenol. The inflection potential in these titrations was found to be 0.585 volts, in the case of aniline as well as *p*-toluidine. These considerations of optimum concentration of amine, temperature and acid strength arrived at for aniline and *p*-toluidine could perhaps be applied to all easily diazotisable primary aromatic amines.

REFERENCES

1. MULLER AND DASCHELT, 1925, *Z. Electrochem.*, **31**, 633.
2. KOLTHOFF AND FURMAN, 1947, *Potentiometric Titrations*, p. 408, John Wiley and Sons.
3. SITARAMAIAH AND SHARMA, 1955, *Curr. Sci.*, **24**, 334.

ON SELF-RECIPROCAL FUNCTIONS--2

BY V. V. L. NARASIMHA RAO

(Banaras Hindu University, Banaras-5)

Received on May 15, 1957

ABSTRACT

In this paper, a Self-Reciprocal function for Hankel Transforms is found out, as product of a finite number of Bessel functions and the same is extended as the number of functions become infinite. A particular case of the above is also verified.

1. We denote a function $f(x)$ as R_μ , if it is self-reciprocal for Hankel Transforms³ of order μ so that it is given by

$$f(x) = \int_0^\infty J_\mu(xy) f(y) \sqrt{xy} dy, \quad (1.1)$$

where $J_\mu(x)$ is a Bessel function of order μ .

2. Bailey¹ has shown that

$$\begin{aligned} & \int_0^\infty J_\rho(bt) \frac{J_\mu(a_1 t) J_\nu(a_2 t) \dots J_k(a_n t)}{t^{\mu+\nu+\dots+k}} \cdot t^{\rho-1} dt \\ &= \frac{2^{\rho-\mu-\nu-\dots-k-1} \Gamma(\rho) a_1^\mu a_2^\nu \dots a_n^k}{b^\rho \Gamma(\mu+1) \Gamma(\nu+1) \dots \Gamma(k+1)}, \end{aligned} \quad (2.1)$$

where $a_1 + a_2 + \dots + a_n < b$, and a_1, a_2, \dots, a_n are all +ve.

Putting $\rho = 1$ and writing y for b , we find that

$$\begin{aligned} & \int_0^\infty J_1(yt) \frac{J_\mu(a_1 t) J_\nu(a_2 t) \dots J_k(a_n t)}{t^{\mu+\nu+\dots+k}} dt \\ &= \frac{2^{-\mu-\nu-\dots-k} a_1^\mu a_2^\nu \dots a_n^k}{y \Gamma(\mu+1) \Gamma(\nu+1) \dots \Gamma(k+1)}, \end{aligned} \quad (2.2)$$

where $a_1 + a_2 + \dots + a_n < y$ and a_1, a_2, \dots, a_n are all +ve.

After a little simplification, we find that (2.2) can be written as:

$$\begin{aligned} & \int_0^\infty J_1(yt) F(t) \sqrt{yt} dt \\ &= \frac{2^{-\mu-\nu-\dots-k} a_1^\mu a_2^\nu \dots a_n^k}{\sqrt{y} \Gamma(\mu+1) \Gamma(\nu+1) \Gamma(k+1)} = \frac{c}{\sqrt{y}}, \end{aligned} \quad (2.3)$$

where

$$F(t) = \frac{J_\mu(a_1 t) J_\nu(a_2 t) \dots J_k(a_n t)}{t^{\mu+\nu+\dots+k} \sqrt{t}},$$

and c is a certain constant.

Dr. Brij Mohan² has shown that the function

$$\frac{1}{\sqrt{x}} \quad (2.4)$$

is R_μ ; and therefore, in particular, it is R_1 .

Therefore from (2.3) and (2.4) we find that the function

$$\frac{J_\mu(a_1 t) J_\nu(a_2 t) \dots J_k(a_n t)}{t^{\mu+\nu+\dots+k} \sqrt{t}} \quad (2.5)$$

is R_1 . It is interesting to note that (2.5) represents a set of Self-Reciprocal functions for different values of a_1, a_2, \dots, a_n , provided $a_1 + a_2 + \dots + a_n$ is always finite. Further, there is no restriction on the values of the constants μ, ν, \dots, k , so that, we obtain different sets of Self-Reciprocal functions for different values of $\mu, \nu \dots k$. All these functions are R_1 .

As a particular case, putting $\mu = 0$ and $n = 1$ in (2.5) we find that

$$\frac{J_0(a_1 t)}{\sqrt{t}} \quad (2.6)$$

is R_1 .

3. Erdelyi⁴ has shown that the functions

$$x^{-\frac{1}{2}} J_{\nu-1}(ax) \quad (3.1)$$

$$\begin{aligned} \text{and } F(x) &= 0; \quad 0 < x < a \\ F(x) &= a^{\nu-1} x^{-\nu+\frac{1}{2}}; \quad a < x < \infty \end{aligned} \quad \left. \right\} \quad (3.2)$$

where $a > 0$; and $R(\nu) > -1$, form a pair of Hankel Transforms of order ν .

Putting $\nu = 1$, we find that the above functions become

$$x^{-\frac{1}{2}} J_0(ax) \quad (3.3)$$

and

$$\left. \begin{aligned} F(x) &= 0; \quad 0 < x < a \\ F(x) &= \frac{1}{\sqrt{x}}; \quad a < x < \infty \end{aligned} \right\} \quad (3.4)$$

respectively, so that

$$\int_0^\infty J_1(xy) \frac{J_0(ax)}{\sqrt{x}} \sqrt{xy} dx = \frac{1}{\sqrt{y}}, \quad (3.5)$$

where $y > a$.

Therefore from (2.4) we find that the function

$$\frac{J_0(ax)}{\sqrt{x}} \quad (3.6)$$

is R_1 , which agrees with the result given in (2.6).

4. Putting $a_1 + a_2 + \dots + a_n < \delta < y$, where δ is any given positive number and writing $\mu_1, \mu_2, \dots, \mu_n$ for μ, ν, \dots, k in (2.5), we find that

$$\frac{J_{\mu_1}(a_1 t) J_{\mu_2}(a_2 t) \dots J_{\mu_n}(a_n t)}{\sqrt{t^{\mu_1 + \mu_2 + \dots + \mu_n}}} \quad (4.1)$$

is R_1 .

Now, since δ is a given positive number, an infinite sequence of positive numbers can be chosen such that

$$a_1 + a_2 + \dots + a_n + \dots \leq \delta. \quad (4.2)$$

Therefore we find that the function

$$\frac{J_{\mu_1}(a_1 t) J_{\mu_2}(a_2 t) \dots J_{\mu_n}(a_n t) \dots}{\sqrt{t^{\mu_1 + \mu_2 + \dots + \mu_n - 1}}} \quad (4.3)$$

is R_1 , where $\mu_1, \mu_2, \dots, \mu_n, \dots$ are any numbers determining the orders of the corresponding Bessel functions.

I thank Dr. Brij Mohan for his help and guidance in the preparation of this paper.

REFERENCES

1. BAILEY, W. N., 1936, "Infinite Integrals Involving Bessel Functions," *Proc. London Mathematical Soc.*, **40**, 47.
2. BRIJ MOHAN, 1935, "A Brief History of Self-Reciprocal Functions," *J. Indian Math. Soc., New Series*, **1** (7), 211.
3. ERDELYI, A., 1954, *Tables of Integral Transforms*, Bateman Manuscripts Project, California Institute of Technology, **2** (McGraw-Hill).
4. —————, 1954, *ibid.*, p. 47.

ANALYTICAL APPLICATION OF ALUMINON TO THE MICRO-DETERMINATION OF IRON III BY THE COLORIMETRIC METHOD

BY ANIL K. MUKHERJI* AND ARUN K. DEY

(*Chemical Laboratories, University of Allahabad, Allahabad*)

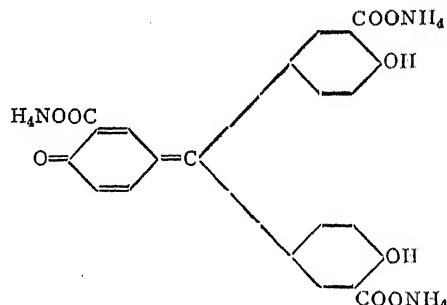
Read at the General Meeting on October 17, 1957

ABSTRACT

The formation of an 1:1 chelate between iron III and ammonium aurintricarboxylate (Aluminon) having λ_{max} at 560 m μ , has been reported. The reagent is sensitive to 1.1 p.p.m. of iron. Beer's law is not obeyed in the range 1.1 to 60 p.p.m., but the colour formed is stable between 20-30° C., at pH 3.2 to 5.4. The reagent can be employed for the colorimetric determination of trivalent iron.

The interference by a large number of cations and anions has been quantitatively studied with Unicam SP 500 Spectrophotometer and the tolerance limits of the foreign ions determined.

AMMONIUM aurintricarboxylate, commonly known as Aluminon, is represented by the following structure:—



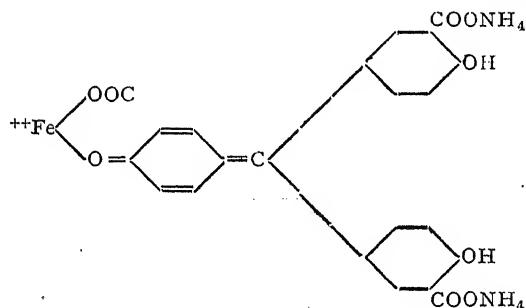
The structure of the compound makes it suitable for yielding metal chelates and the reagent has found application in the colorimetric determination of aluminium,¹ including the estimation of the metal in commercial materials and alloys.² Bobtelsky and Ben-Basset³ employed Aluminon for the determination of iron, aluminium and chromium, by the heterometric method developed by them. Recently, Mukherji and Dey⁴ reported the formation of coloured lakes of various inorganic cations with this reagent

* Present Address: Coates Chemical Laboratory, Louisiana State University, Baton Rouge 3, La., U.S.A.

and suggested further applications of Aluminon to colorimetric analysis. They have made a detailed study of metal chelates involving ammonium aurintricarboxylate, including those of copper II,⁵ uranyl II⁶ and thorium IV⁷ and have been able to make use of the colour formation in the micro-determination of these metals.^{8, 9}

In a number of communications, Dey and coworkers¹⁰ have reported their search for new reagents for the colorimetric determination of various metals, especially of the rarer ones. They have, in this connection, tried Alizarin Red S,¹¹ Chromotropic acid,¹² Rhodizonic Acid,¹³ Quinalizarin,¹⁴ *p*-dimethyl amino-benzal-Rhodanine,¹⁵ 2:4 hydroxy-5-chloro-acetophenone¹⁶ and dithioxamide,¹⁷ for this purpose.

Mukherji and Dey¹⁸ have observed that iron III forms an 1:1 chelate with ammonium aurintricarboxylate, having λ_{max} at 560 m μ . They have determined the composition, stability, and free energy of formation of the chelate and have assigned the following structure to the chelate:—



In this paper we have described our experiments on the use of Aluminon in the determination of trivalent iron, when present in small amounts, using the colorimetric method.

EXPERIMENTAL

Materials

Solutions of ferric chloride (BDH AnalaR) and of ammonium aurintricarboxylate were prepared and standardised by the usual methods. Since the quality of Aluminon employed is of importance, BDH Reagent was used, prepared by the method of Smith, Sager and Siewers,¹⁹ as ascertained from the manufacturers.²⁰ All other chemicals used were of reagent grade.

Procedure

For optical measurements Unicam SP 500 Spectrophotometer was used with 10 mm. glass cells supplied by the manufacturers. Where necessary,

Klett-Summerson's Photo-electric Colorimeter was employed with Klett Colour Filters. The solutions were taken in Klett tubes of standard and uniform diameter. pH measurements were done using L & N pH meter operated by 220 volts/50 cycle mains, using glass and calomel electrode system supplied with the instrument. All experiments were conducted in an air-conditioned room, maintaining a constant temperature of 25° C.

Validity of Beer's Law

To a fixed volume of the reagent solution were added varying volumes of ferric chloride solution, the total volumes raised to 50 ml. by the addition of water and allowed to stand for 15 minutes to attain equilibrium. The colour intensity was measured with the Spectrophotometer, or with the colorimeter, as necessary. Beer's law is not obeyed in the range of concentration from 1.1 to 60 p.p.m. of iron, as may be seen from some of the typical results given in the tables below.

TABLE I

Concentration of ferric chloride	= 0.0001 M
Concentration of Aluminon	= 0.0004 M
Volume of the reagent taken	= 20 ml.
Total Volume	= 50 ml.

Volume of FeCl_3 ml.	Optical density		
	450 m μ	500 m μ	550 m μ
0	0.100	0.145	0.100
2	0.120	0.180	0.160
4	0.150	0.215	0.220
6	0.160	0.230	0.240
8	0.180	0.250	0.240
10	0.190	0.260	0.280
12	0.205	0.270	0.300
14	0.215	0.280	0.310
16	0.220	0.290	0.320
18	0.220	0.290	0.320

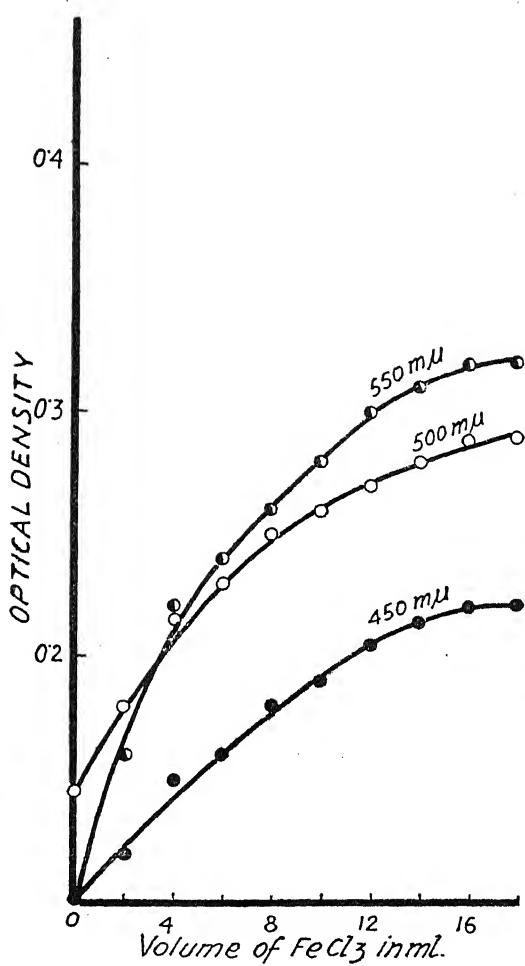


FIG. 1. FeCl_3 -Aluminon system.

TABLE II

Concentration of ferric chloride = 0.0001 M
 Concentration of Aluminon = 0.001 M
 Volume of the reagent taken = 20 ml.
 Total volume = 50 ml.

Volume of FeCl_3 ml.	Optical density		
	450 m μ	500 m μ	550 m μ
0	0.195	0.290	0.180
2	0.250	0.360	0.300
4	0.310	0.420	0.420
6	0.350	0.470	0.490
8	0.380	0.500	0.540
10	0.400	0.530	0.580
12	0.420	0.560	0.620
14	0.440	0.590	0.660
16	0.460	0.620	0.700
18	0.470	0.640	0.740

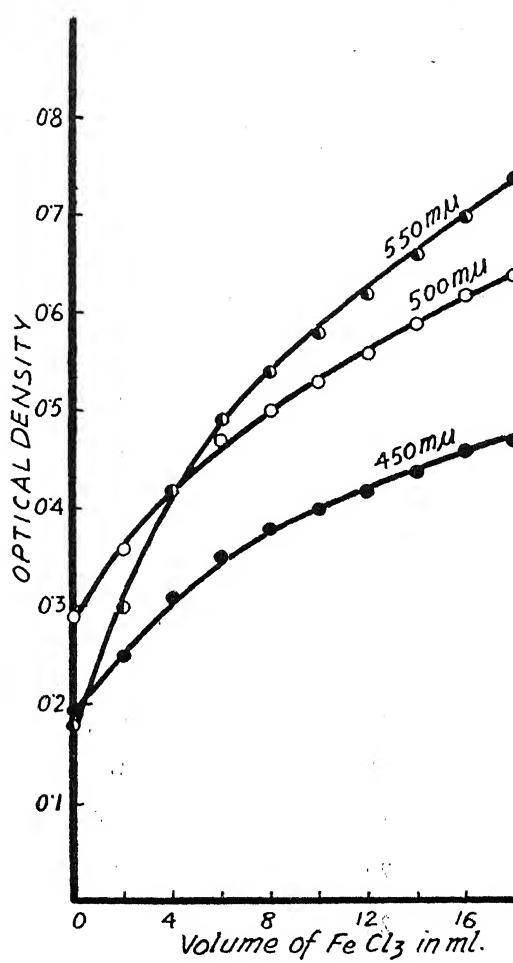


FIG. 2. FeCl_3 -Aluminon system.

TABLE III

Concentration of ferric chloride = 0.0001 M
 Concentration of Aluminon = 0.001 M
 Volume of the reagent taken = 10 ml.
 Total volume = 50 ml.
 Filter used No. 50 Green, Transmission = 470-530 m μ

(Fig. 3, Curve B)

Volume of FeCl_3 ml.	Colorimeter reading
0	108
2	139
4	170
6	193
8	216
10	234
12	250
14	269
16	276
18	286
20	300
22	310
24	320
26	324

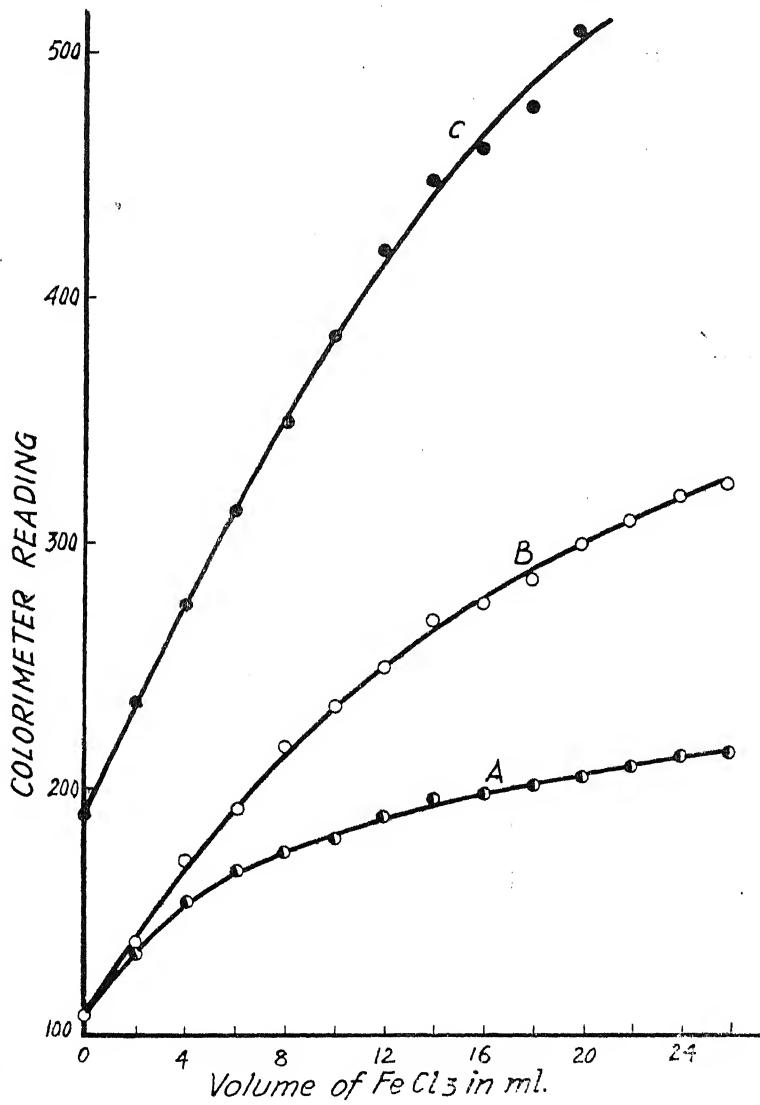


FIG. 3. FeCl_3 -Aluminon system.

TABLE IV

Concentration of ferric chloride = 0.00005 M
 Concentration of Aluminon = 0.001 M
 Volume of the reagent taken = 10 ml.
 Total volume = 50 ml.
 Filter used No. 50 Green, Transmission = 470-530 m μ

(Fig. 3, Curve A)

Volume of FeCl_3 ml.	Colorimeter reading
0	108
2	135
4	155
6	167
8	175
10	180
12	190
14	198
16	199
18	202
20	205
22	210
24	214
26	214

TABLE V

Concentration of ferric chloride = 0.0001 M
Concentration of Aluminon = 0.002 M
Volume of the reagent taken = 10 ml.
Total volume = 50 ml.
Filter used No. 50 Green, Transmission = 470-530 m μ

(Fig. 3, Curve C)

Volume of FeCl_3 ml.	Colorimeter reading
0	190
2	237
4	276
6	315
8	350
10	385
12	420
14	450
16	462
18	478
20	510

Stability of the colour at room temperature

The colour is stable at room temperature. A solution of 0.00002 M in Fe^{+3} and 0.0001 M in Aluminon at a pH of 5.0, gave exactly the same optical density of 0.39 per cm. at 540 m μ , even after 72 hours of standing at room temperature.

Influence of temperature

The colour intensity was found to be stable up to 30° C. Further rise of temperature causes a decrease in optical density and the lake has a tendency to separate out.

TABLE VI

Concentration of ferric chloride	= 0.00002 M
Concentration of Aluminon	= 0.0001 M
pH of the mixtures	= 5.00
Temperature °C.	.. 20 25 30 35 40 45
Optical density per cm. (540 m μ)	0.390 0.390 0.390 0.385 0.370 0.365

Influence of pH

The colour was found to be stable between pH 3.2 to 5.4, as may be seen below:—

TABLE VII

Concentration of ferric chloride	= 0.00005 M
Concentration of Aluminon	= 0.0002 M
Temperature	= 25° C.
pH	.. 2.50 3.20 4.50 4.80 5.40 8.80 10.20
Optical density per cm. (540 m μ)	0.820 0.860 0.860 0.860 0.860 0.720 0.520

Sensitivity of the reagent

The smallest amount of iron III that can be detected with Aluminon is 1.1 p.p.m.

Influence of foreign ions

The effect of a large number of cations and anions on the intensity of colour was quantitatively studied with the spectrophotometer and the tolerance limits were determined. The tolerance limit denotes the concentration of a foreign ion which affects the optical density by not more than $\pm 2\%$. The results are shown in Table VIII.

TABLE VIII

Concentration of ferric chloride	= 0.00002 M (1.1 p.p.m.)
Concentration of Aluminon	= 0.001 M
pH of the mixtures	= 5.00 ± 0.50
Temperature	= 25° C.

Ion	Added as	Concentration of ion (p.p.m.)	Observed change in optical density %	Tolerance limit (p.p.m.)
Ag^+	AgNO_3	43	+2.5	
		30	+2	30
Tl^+	Tl_2SO_4	163	+3	
		60	+1.5	60
Pb^{+2}	$\text{Pb}(\text{NO}_3)_2$	83	+8	
		5	+1.5	5
Hg_2^{+2}	$\text{Hg}_2(\text{NO}_3)_2$	160	-7.5	
		20	-1.5	20
Hg^{+2}	HgCl_2	80	-5	
		30	-2	30
Cu^{+2}	CuSO_4	Interferes at all concentrations	0	
Bi^{+3}	Bi-oxal	80	Turbid	0
Cd^{+2}	CdCl_2	90	+3	
		45	+2	45
AsO_3^{-3}	H_3AsO_3	125	-5	
		25	-1.5	25
Sb^{+3}	SbCl_3	57	Turbid	0
Fe^{+2}	Fe am sulph	Interferes at all concentrations	0	
Al^{+3}	$\text{Al}(\text{NO}_3)_3$	Interferes at all concentrations	0	
Cr^{+3}	CrCl_3	Interferes at all concentrations	0	
Mn^{+2}	MnSO_4	220	+3	
		110	+1.5	Large excess
Zn^{+2}	ZnSO_4	260	+3	
		130	+1.5	Large excess

TABLE VIII—*Contd.*

Ion	Added as	Concentration of ion (p.p.m.)	Observed change in optical density %	Tolerance limit (p.p.m.)
Ni^{+2}	NiSO_4	115 75	+3 +2	75
Co^{+3}	CoSO_4	115 75	+3 +2	75
Ba^{+2}	BaCl_2	80 60	+3 +2	60
Sr^{+2}	SrCl_2	70 35	+4 +2	35
Ca^{+2}	$\text{Ca}(\text{NO}_3)_2$	40 20	+4 +2	20
Mg^{+2}	MgSO_4	20 15	+3 +2	15
Be^{+2}	BeSO_4	Interferes at all concentrations	0	
UO_2^{+2}	UO_2SO_4	Interferes at all concentrations	0	
Th^{+4}	ThCl_4	Interferes at all concentrations	0	
Zr^{+4}	$\text{ZrO}(\text{NO}_3)_2$	Interferes at all concentrations	0	
Ce^{+3}	$\text{Ce}_2(\text{SO}_4)_3$	Interferes at all concentrations	0	
Ce^{+4}	$\text{Ce}(\text{SO}_4)_2$	Interferes at all concentrations	0	
WO_4^{-2}	Na_2WO_4	10	-7.5	0
MoO_4^{-2}	$(\text{NH}_4)_2\text{MoO}_4$	7	-7	0
VO_3^-	NH_4VO_3	2	-10	2
SeO_4^{-2}	K_2SeO_4	114 57	+3 +1.5	
TeO_3^{-2}	K_2TeO_3	70 10	-10 -1.5	57 10

TABLE VIII—*Contd.*

Ion	Added as	Concentration of ion (p.p.m.)	Observed change in optical density %	Tolerance limit (p.p.m.)
CO_3^{2-}	Na_2CO_3	24 18	—2.5 —2	18
SO_4^{2-}	K_2SO_4	140	—0.5	Large excess
Cl^-	KCl	280 140	—2.5 —1.5	Large excess
Br^-	KBr	320 160	—2 —1	Large excess
I^-	KI	500 200	—3 —1	Large excess
ClO_3^-	KClO_3	430 150	—3 —1	Large excess
BrO_3^-	KBrO_3	500 200	—3 —1	Large excess
IO_3^-	KIO_3	700 200	—3 —0.5	Large excess
F^-	NaF	76 8	—10 —2	8
SiO_3^{2-}	Na_2SiO_3	200 90	—3 —1.5	90
Citrate	Na ₂ Cit	76 30	—5 —2	30
Tartrate	Na ₂ Tart	60 24	—5 —2	24
Oxalate	NH_4Oxal	35 10	—5 —2	10
NO_3^-	KNO_3	200	—1.5	Large excess
CNS [—]	KCNS	50	—1	50

TABLE VIII—*Contd.*

Ion	Added as	Concentration of ion (p.p.m.)	Observed change in optical density %	Tolerance limit (p.p.m.)
PO_4^{3-}	Na_2HPO_4	35	—3	
		20	—2	20
$\text{S}_2\text{O}_8^{2-}$	$\text{K}_2\text{S}_2\text{O}_8$	100	—3	
		70	—2	70
HCO_3^-	NaHCO_3	24	—3	
		12	—1.5	12
$\text{S}_2\text{O}_3^{2-}$	$\text{Na}_2\text{S}_2\text{O}_3$	90	—4	
		45	—2	45
Acetate	NaAc	50	—2.5	
		30	—2	30
$\text{B}_4\text{O}_7^{2-}$	$\text{Na}_2\text{B}_4\text{O}_7$	49	—10	
		8	—2	8

PROCEDURE RECOMMENDED

Though Beer's law is not obeyed by the system, yet the colour formed is stable and reproducible and Aluminon may be recommended in the colorimetric determination of iron. The iron salt should be in the trivalent state. A calibration curve has first to be obtained showing the variation of colour with different amounts of ferric salt with a large excess of the reagent. The pure iron salt, as chloride, sulphate or nitrate should then be treated directly or in an aliquot portion, with the same amount of the reagent as in the calibration curve. The reagent should be in fifty-fold molar excess, and the solution should be freshly prepared. The pH should be adjusted to 5.00 ± 0.50 and the temperature of observation between 20 and 30°C . The optical density of the solution may be read at $540\text{ m}\mu$ in a spectrophotometer, using a glass cell of suitable thickness, and the concentration determined from the calibration curve. The colour intensity may also be determined with a photoelectric colorimeter using an appropriate green filter.

REFERENCES

1. JOHNSON, W. C., 1955, *Organic Reagents for Metals*, Chemical Publishing Co. Inc., New York.

2. BANERJEE, D. K., 1957, *Analyt. Chem.*, **29**, 55.
3. BOBTESKY, M. AND BEN-BASSET, A., 1956, *Anal. Chem. Acta*, **14**, 439.
4. MUKHERJI, A. K. AND DEY, A. K., 1956, *Z. anal. Chem.*, **152**, 424.
5. —————, 1958, *Anal. Chim. Acta*, **18** (In Press).
6. —————, 1958, *J. Inorg. Nucl. Chem.*, **5** (In Press).
7. —————, *J. Sci. Ind. Res., India* (Under publication).
8. —————, 1958, *Anal. Chim. Acta*, **18** (In Press).
9. —————, 1958, *Proc. Ind. Sci. Cong.*, **45** (Symposium on Microchemistry).
10. —————, 1957, *ibid.*, **44** (3), 70.
11. —————, 1957, *Proc. Nat. Acad. Sci., India*, **26A**, 20.
12. MATHUR, K. C. AND DEY, A. K., 1957, *Z. anal. Chem.*, **154**, 347.
13. MUKHERJI, A. K. AND DEY, A. K., 1957, *Chim. Anal.*, **39**, 149.
14. —————, 1957, *Z. anal. Chem.*, **55**, 417.
15. BANERJI, S. K. AND DEY, A. K., 1958, *Proc. Ind. Sci. Congr.*, **45** (3), 150.
16. —————, 1957, *Z. anal. Chem.* (In Press).
17. —————, 1958, *J. prakt. Chem.* (In Press).
18. MUKHERJI, A. K., AND DEY, A. K. 1958, *J. Ind. Chem. Soc.*, **35** (In Press).
19. SMITH, W. H., SAGER, E. E. AND SIEWERS, I. J., 1949, *Analyt. Chem.*, **21**, 1334.
20. BRITISH DRUG HOUSES LTD., POOLE (December 1956), *Private Communication*.

SEPARATION OF AMINO ACIDS AFTER PHOTO-
CHEMICALLY SYNTHESISING THEM FROM
A MIXTURE OF PARAFORMALDEHYDE,
POTASSIUM NITRATE AND WATER

BY KRISHNA BAHADUR AND S. RANGANAYAKI

(*Department of Chemistry, University of Allahabad, Allahabad*)

Received on November 26, 1956

IN a previous paper¹ it has been mentioned that a number of amino acids are formed in a mixture of paraformaldehyde, potassium nitrate and water if a little of ferric chloride is used as a catalyst and the mixture is exposed to sunlight. We have seen that artificial light from ordinary electric lamp is also effective in this synthesis. We have been able to separate some of these amino acids by chemical methods and to study their chemical and physical properties.

10 g. of paraformaldehyde and 1 g. of potassium nitrate were taken in a 1.51 Pyrex beaker. To these 100 c.c. of distilled water and 10 c.c. of 6 N ferric chloride solution were added. The beaker was covered with a Pyrex beaker cover and the mixture was exposed to 500 watts electric light, keeping the bulb 2 ft. above the beaker. The exposure was continued for 800 hours, stirring the mixture with a glass rod once in 24 hours. The temperature variation of the solution during the period of exposure was between 25 and 30.5° C.

During the exposure the whole of paraformaldehyde disappeared and a pale yellow colloidal solution was formed. This solution indicated the presence of leucine, tyrosine, proline, glutamic acid, aspartic acid, histidine, arginine, alanine, phenylalanine, asparagine and serine. These amino acids were chemically separated from the above aqueous mixture according to the following scheme:

I. The exposed solution was evaporated to 250 c.c. on a water-bath and filtered. The precipitate was kept for further examination.

II. The filtrate of I was extracted with aqueous butyl alcohol to separate monoamino mono-carboxylic amino acid.² It was mixed with about 250 c.c. of aqueous butyl alcohol and the mixture was shaken for sometimes. It was then allowed to stand in a separating funnel overnight.

Next day the butyl alcohol layer was separated and the aqueous solution was again extracted with two 100 c.c. portions of aqueous butyl alcohol as described above. The butyl alcohol layer thus separated was evaporated to dryness, on a water-bath and a residue was obtained.

III. The residue of II was extracted with absolute ethyl alcohol in which proline is soluble and other monoamino mono-carboxylic acids are insoluble. The soluble portion was separated by filtration. The insoluble part was washed twice with small amounts of absolute ethyl alcohol to remove the whole of the proline. The alcoholic filtrate was evaporated to dryness on water-bath. This gave a residue of 0.005 g. and was tested and found to be proline. The insoluble portion was kept for the separation of the other monoamino mono-carboxylic acids.

IV. The aqueous portion of II was treated with excess of barium hydroxide and boiled for 15 minutes. A brown precipitate appeared which was filtered off. This precipitate was of ferric hydroxide. This precipitation of the ferric ions was complete as the filtrate did not indicate presence of iron. The precipitate was rejected. The filtrate was concentrated to 40 c.c. and to it was added 400 c.c. of absolute ethyl alcohol. A thick precipitate was formed. The precipitate which was suspected to be a mixture of barium aspartate and barium glutamate^{3,4} was filtered. The precipitate was tested and found to be barium aspartate and glutamate and the filtrate contained barium salts of the amino acids.

V. The barium aspartate and glutamate precipitate of IV was dried in hot air, dissolved in minimum amount of water and reprecipitated with absolute ethyl alcohol. The precipitate thus obtained was filtered, dried, and redissolved in distilled water. Barium of the barium salts of the amino acids was quantitatively precipitated by the addition of calculated amount of standard dilute sulphuric acid. The mixture was boiled for 15 minutes and filtered. The precipitate thus obtained was that of barium sulphate and rejected. To the filtrate was added solid copper carbonate till there was no effervescence. A little excess of copper carbonate was added and the mixture was boiled for 15 minutes and filtered. The precipitate is that of excess of copper carbonate and copper aspartate and the solution contains copper glutamate.⁵

VI. The precipitate of V was washed with a little cold distilled water and suspended in water. To it was added a little dilute sulphuric acid and hydrogen sulphide was passed through this till the whole of the copper precipitated as copper sulphide and the copper salt of the amino acid was

completely decomposed. The mixture was filtered. The black precipitate of copper sulphide was rejected. The filtrate contained free aspartic acid and dilute sulphuric acid.

VII. To the filtrate of VI was added excess of barium hydroxide and the mixture was boiled for 10 minutes. The free sulphuric acid of the filtrate was converted into insoluble barium sulphate and soluble barium aspartate was formed in the solution. The mixture was filtered and the precipitate of barium sulphate was rejected. The filtrate was concentrated to 20 c.c. and to it was added 200 c.c. of absolute ethyl alcohol. Barium aspartate was precipitated.

Above precipitate was separated by filtration, washed with absolute alcohol, dried, redissolved in least amount of distilled water and reprecipitated with the addition of absolute ethyl alcohol. The precipitate obtained was filtered, washed with absolute alcohol and dried in dry air.

This precipitate was dissolved in 200 c.c. of distilled water and the barium present was completely precipitated by adding quantitative sulphuric acid. The mixture was boiled for 15 minutes to complete the precipitation, filtered, and the precipitate of barium sulphate was rejected. The solution contained aspartic acid. This was dried on water-bath. An oily liquid was obtained which on drying with alcohol changed into a white residue. This residue was 0.312 g. in weight and was tested and found to be aspartic acid.

VIII. The filtrate of VI contained copper salt of glutamic acid. To it was added a little of dilute sulphuric acid and hydrogen sulphide was passed till the whole of the copper salt completely decomposed. The mixture was filtered to remove the black precipitate of copper sulphide. The filtrate was made alkaline by the addition of excess of barium hydroxide. This converted the free sulphuric acid of the solution into insoluble barium sulphate and soluble barium glutamate was formed in the solution.

The mixture was boiled for 10 minutes and filtered. The precipitate of barium sulphate was rejected and the filtrate was concentrated to 20 c.c. To this was added excess of absolute ethyl alcohol which precipitated barium glutamate. The mixture was kept overnight for complete precipitation of barium glutamate. Next day the precipitate was filtered off, washed with absolute alcohol, dried in air, redissolved in least quantity of water and reprecipitated with absolute alcohol as mentioned before.

The above precipitate was dissolved in 200 c.c. of water and its barium was precipitated as barium sulphate by the quantitative addition of sul-

phuric acid. The mixture was boiled for a few minutes and filtered. The precipitate was rejected and the filtrate was evaporated on a water-bath. First an oily substance was formed which on repeated drying with the addition of alcohol changed into a solid residue. This residue weighed 0.122 g. and was tested and found to be glutamic acid.

IX. The filtrate of IV was concentrated on a water-bath and to it was added dilute sulphuric acid till the precipitation of barium sulphate was complete. The mixture was boiled for 15 minutes, and filtered. The precipitate was rejected and to the filtrate was added solid copper carbonate till the effervescence ceased. A little more of copper carbonate was added to it and the mixture boiled for 10 minutes and filtered. The precipitate was tested for the insoluble copper salt of amino acids and the filtrate for the soluble copper salts of the amino acids. Other than these the above precipitate contained some unused copper carbonate and the filtrate, some, copper sulphate.

X. The precipitate of IX was washed with distilled water. This was then suspended in water, a little of dilute sulphuric acid was added to this suspension and hydrogen sulphide was passed through it to decompose the copper salts and to precipitate the copper present as copper sulphide. After complete precipitation of copper sulphide, the mixture was filtered. The precipitate was rejected and the filtrate boiled to remove the excess of hydrogen sulphide. To this solution was added excess of barium hydroxide solution and the solution was boiled. The free sulphuric acid of the solution was thus precipitated as barium sulphate. The mixture was filtered and the precipitate was rejected. The solution was concentrated on a water-bath and to it was added quantitative sulphuric acid to remove the barium of the barium hydroxide and barium salts of the amino acids as barium sulphate. The mixture was boiled for 15 minutes and filtered. The precipitate was rejected and filtrate was kept for further separation of amino acids.

XI. The filtrate of X was boiled with excess of freshly precipitated zinc hydroxide for 30 minutes and filtered. The precipitate contained excess of zinc hydroxide and those zinc salts of the amino acids present in the solution which are insoluble in water. The filtrate contained soluble zinc salts of the amino acids present in this solution.

XII. The precipitate of XI was washed with distilled water, suspended in water and through this was passed hydrogen sulphide until the whole of the zinc hydroxide was converted to zinc sulphide and zinc salt of the

amino acid was decomposed. The mixture was filtered and the precipitate of zinc sulphide was rejected. The filtrate on drying over water-bath gave an oily liquid. Several attempts to dry it with ethyl alcohol gave only a semi dry-product. To this was added 15 drops of concentrated hydrochloric acid and the mixture on evaporating on water-bath gave a white solid residue which weighed 0.2080 g. This residue was tested and found to be leucine hydrochloride.

XIII. Through the filtrate of XI was passed hydrogen sulphide to completely decompose the zinc salts of amino acids. The mixture was filtered. The precipitate of zinc sulphide was rejected and filtrate was boiled to remove excess of hydrogen sulphide and then concentrated over a water-bath to 50 c.c. To this was added 100 c.c. of 95 per cent. ethyl alcohol and the solution again concentrated and kept for crystallisation. Crystals appeared in this solution in 24 hours. These were separated by filtration. The filtrate was kept for further analysis and the crystals were washed with absolute ethyl alcohol, dried and weighed. This weighed 0.0696 g. By round paper chromatography this was found to be a mixture of two amino acids. These were separated by Chromatographic Method⁶ and gave 0.0320 g. of valine and 0.034 g. of asparagine.

XIV. The filtrate of XIII on drying on a water-bath gave a residue of 0.0296 g. This residue on further testing was found to be of phenylalanine.

XV. The filtrate of IX was acidified with a little of dilute hydrochloric acid and hydrogen sulphide was passed into it until the whole of copper salt of amino acids was decomposed and the copper in the solution was converted to copper sulphide. The mixture was filtered and the precipitate was rejected. The filtrate was boiled to remove excess of hydrogen sulphide, concentrated over a water-bath and kept for crystallisation. Beautiful crystals separated in 24 hours. These crystals gave the tests of amino acids and were kept for further analysis. After removing these crystals by filtration, the filtrate was boiled with excess of freshly precipitated zinc hydroxide for 30 minutes. The mixture was filtered. The precipitate was that of excess of zinc hydroxide and rejected. To the filtrate was added aqueous solution of mercuric chloride. A thick white precipitate appeared. After adding sufficient mercuric chloride for complete precipitation the mixture was filtered.

XVI. The precipitate of XV obtained by the addition of mercuric chloride was washed with distilled water, suspended in water, mixed with a little of dilute hydrochloric acid and into this was passed hydrogen sulphide till

the mercuric salt of the amino acid was completely decomposed. The black precipitate of mercuric sulphide thus formed was separated by filtration and the filtrate was boiled for sometime to remove excess of hydrogen sulphide and then dried on a water-bath. A pale yellow residue was obtained which weighed 0.132 g. This was tested and found to be histidine hydrochloride.

XVII. Through the filtrate of XV was passed hydrogen sulphide. Black precipitate of mercuric sulphide appeared. After the complete precipitation of mercuric ions as mercuric sulphide the mixture was filtered. The precipitate was rejected and the filtrate was evaporated to dryness on a water-bath. To the residue was added a few c.c. of distilled water and it was again evaporated to dryness. The process was repeated a few times to be sure that no free hydrochloric acid was present in the residue. It was then dissolved in 50 c.c. of distilled water and through this solution was passed hydrogen sulphide. White precipitate of zinc sulphide appeared which on complete precipitation was filtered off and rejected.

XVIII. The filtrate of XVII was boiled for 10 minutes to remove excess of hydrogen sulphide, and then evaporated to dryness on a water-bath. This residue was dissolved in distilled water and to this solution was added silver nitrate solution. A white precipitate appeared. Excess of silver nitrate solution was added to this solution for the complete precipitation and then the precipitate was separated by filtration. Both the filtrate and precipitate were subjected to further analysis.

XIX. The precipitate of XVIII was washed with distilled water, suspended in 100 c.c. of distilled water and to it was added a large excess of concentrated ammonium hydroxide. About two-third of the precipitate dissolved in it and one-third remained insoluble. The soluble fraction was found to be silver chloride and insoluble portion was silver salt of an amino-acid. The insoluble portion was separated by filtration, washed first with concentrated ammonium hydroxide and then with distilled water. The insoluble material was then suspended in water and through it was passed hydrogen sulphide. The silver salt was decomposed and a black precipitate of silver sulphide was formed. After complete precipitation the mixture was filtered and the precipitate was rejected. The filtrate was boiled for a few minutes to remove excess of hydrogen sulphide and then evaporated to dryness on a water-bath with a little hydrochloric acid. A pale yellow residue was obtained. This weighed 0.094 g. and was tested and found to be arginine hydrochloride.

XX. To the filtrate of XVIII was added potassium hydroxide solution until its pH became 7. Then to it was added phosphotungstic acid solution. A pale voluminous precipitate was formed. Enough of phosphotungstic acid solution was added to complete the precipitation. The mixture was then filtered and the precipitate and filtrate were kept for further analysis.

XXI. The precipitate of XX was washed with water, suspended in about 50 c.c. of distilled water, made alkaline with ammonia and hydrogen sulphide was passed into it until no more precipitate appeared. The solution was filtered and the precipitate rejected. The filtrate was evaporated to dryness on a water-bath. The residue was dissolved in water, and to it was added excess of barium hydroxide solution. A white precipitate of barium phosphate was obtained which was filtered off and removed. The excess of barium hydroxide of the solution was reacted with quantitative sulphuric acid and the barium sulphate thus formed was filtered off and removed. The filtrate was evaporated to dryness on a water-bath and a residue weighing 0.052 g. was obtained. This residue was tested and found to be lysine.

XXII. To see whether the crystals of amino acids obtained in XV were those of only tyrosine hydrochloride or a mixture of tryptophane hydrochloride also, a little of this was dissolved in water and to this solution was added an aqueous solution of mercuric chloride. No precipitate was obtained and so the possibility of this being mixed with tryptophane was eliminated. The total weight of the above crystals was 0.2200 g. It was tested and found to be tyrosine hydrochloride.

XXIII. The portion of III which was insoluble in absolute alcohol weighed 0.102 g. This was tested with round paper chromatography and was found to contain a little of leucine and enough of serine and traces of threonine. Their quantities being very small no attempt of separating leucine and threonine was made. Serine was however separated by Giri's Round Paper Chromatographic Method⁶ and a product of 0.0708 g. was obtained which was tested and found to be serine.

XXIV. The precipitate of I was extracted with aqueous butyl alcohol. The butyl alcohol layer was separated and evaporated to dryness on a water-bath. The portion insoluble in aqueous butyl alcohol was kept for further analysis. The residue obtained by the evaporation of the butyl alcohol layer was extracted with glacial acetic acid. A part of it dissolved in this and a part remained insoluble. These portions were separated by filtration and the filtrate was evaporated to dryness. The portion which was soluble in glacial acetic acid weighed 0.0425 g. and was tested and

found to be leucine. The part insoluble in glacial acetic acid weighed 0.0184 g. and was tested and found to be tyrosine.

XXV. The portion of XXIV which was insoluble in aqueous butyl alcohol was extracted with excess of hot water. The residue was then rejected and the aqueous solution was evaporated to dryness on a water-bath. A residue was obtained. This residue was treated with glacial acetic acid. It separated into an acetic acid-soluble and an acetic acid-insoluble portion. The soluble portion weighed 0.021 g. and was identified as leucine and the portion insoluble in acetic acid weighed 0.0982 g. and it was found to be tyrosine.

Confirmatory tests for the amino acids isolated in the above analysis.

Proline.—Decomposition point 202° C. Gave a picrate of M.P. 136° C. Soluble in aqueous butyl alcohol and absolute ethyl alcohol. Does not give out nitrogen on treatment with nitrous acid.

Leucine.—Decomposition point 330° C. Copper salt is insoluble in water. Gives hydantoic acid of M.P. 188° C. and phenylurea of M.P. 165° C.

Phenylalanine.—Decomposition point 273° C. Sparingly soluble in cold water and insoluble in alcohol. On gentle heating gives phenyl-lactimide, M.P. 290° C.

Valine.—Decomposition point 297° C. On gentle heating gives anhydride, M.P. 303° C. Copper salt is sparingly soluble in water. Gives phenylurea, M.P. 163° C.

Aspartic acid.—Decomposition point 268° C. Insoluble in alcohol. Barium salt is insoluble in alcohol. Gives hydantoic acid, M.P. 162° C. Copper salt is insoluble in water.

Glutamic acid.—Decomposition point 225° C. Copper salt is insoluble in water. Insoluble in alcohol. Hydrochloride is insoluble in cold concentrated hydrochloric acid. Hydantoic acid, M.P. 150° C.

Alanine.—Decomposition point 294° C. Insoluble in alcohol. On warming with PbO_2 yields acetaldehyde and ammonia. Copper salt soluble in water. Phenyl-urea, M.P. 190° C.

Lysine.—Decomposition point 224° C. Copper salt is soluble in water. Forms soluble zinc salt. Gives precipitate with phosphotungstic acid. Phenyl-urea, M.P. 183° C.

Arginine.—Decomposition point 237° C. Copper and zinc salt soluble in water. Gives precipitate with phosphotungstic acid. Forms a picrate, M.P. 201° C.

Tyrosine.—Decomposition point 318° C. Copper salt is insoluble in water. On fusion with sodium hydroxide gives *p*-hydroxybenzoic acid, M.P. 213° C. Hydantoic acid derivative decomposes at 216° C.

Histidine.—Decomposition point 275° C. Yields a picrate, M.P. 86° C. Copper and zinc salts are soluble in water. Forms an insoluble salt with mercuric chloride.

Serine.—Decomposition point 228° C. On boiling with sulphuric acid gives ammonia and pyruvic acid. With nitrous acid gives glyceric acid and acetaldehyde. Oxidises to glycolaldehyde with periodic acid. Phenyl-urea, M.P. 168° C.

Asparagine.—Decomposition point 226° C. On boiling with dilute alkali yields ammonia and aspartic acid. Copper salt is insoluble in cold water. Picrate decomposes at 180° C.

REFERENCES

1. BAHADUR, K., 1954, *Nature*, **173**, 1141, June 12.
2. DAKIN, H. D., 1918, *Biochem. J.*, **12**, 209; 1920, *J. Biol. Chem.*, **44**, 499; 1923, *Z. Physiol. Chem.*, **130**, 159.
3. FOREMAN, F. W., 1914, *Biochem. J.*, **8**, 463.
4. JONES, D. B. AND MOELLER, O., 1928, *J. Biol. Chem.*, **79**, 429.
5. BRAZIER, M. A. B., 1930, *Biochem. J.*, **24**, 1188.
6. GIRI, K. V. AND PRASAD, A. L. N., 1951, *Nature*, **168**, 786.

EDITORIAL BOARD

1. PROF. P. S. GILL, Aligarh (*Chairman*).
2. „, K. BANERJI, Allahabad.
3. „, RAM BEHARI, Delhi.
4. „, P. L. SRIVASTAVA, Allahabad.
5. „, S. GHOSIT, Allahabad.
6. „, A. K. BHATTACHARYA, Saugor.
7. „, N. R. DHAR, Allahabad.
8. „, S. RANJAN, Allahabad.
9. „, R. MISRA, Banaras.
10. „, M. D. L. SRIVASTAVA, Allahabad.
11. „, W. D. WEST, Saugor.
12. DR. S. P. RAYCHAUDHURI, New Delhi.
13. „, R. K. SAKSENA, Allahabad.
14. „, R. N. TANDON, Allahabad (*Secretary*).

CONTENTS

	PAGE
Corona Relationship under Low Frequency Silent Electric Discharge	D. P. Jatar and H. D. Sharma
	87
Studies in Coagulation. Part VII. Nature of Hydrous Stannic Oxide and Coagulation of Its Positive Sol	Rama Shanker Rai and Satyeshwar Ghosh
	94
Physico-Chemical Studies in the Formation of Cuprammonium Compounds. Part II. Composition of Cupric-Ammino Nitrates	Arun K. Dey
	98
Physico-Chemical Studies in the Formation of Cuprammonium Compounds. Part III. Composition of Cupric-Ammino Chlorides	Arun K. Dey
	103
Adsorption of Phosphates by a Calcareous Sand	N. R. Dhar and S. G. Misra
	106
Characterisation of the Gamma Function.	D. P. Banerjee
	112
Some Relations between Special Functions	B. B. Misra
	117
Behaviour of Alkali Soils in Fixing Monocalcium Phosphate from Solutions	N. R. Dhar and S. G. Misra
	120
Physico-Chemical Studies in the Formation of Complex Stannioxalates. Part V. Spectroscopic Study of the System: $\text{SnCl}_4\text{-K}_2\text{C}_2\text{O}_4$	Arun K. Dey
	126
Potentiometric Determination of Aromatic Amines by the Diazo Reaction	G. Sitaramaiah and R. S. Sharma
	129
On Self-Reciprocal Functions—2	V. V. L. Narasimha Rao
	134
Analytical Application of Aluminon to the Micro-Determination of Iron III by the Colorimetric Method	Anil K. Mukherji and Arun K. Dey
	138
Separation of Amino Acids after Photo-Chemically Synthesising them from a Mixture of Paraformaldehyde, Potassium Nitrate and Water	Krishna Bahadur and S. Ranganayaki
	154